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Exposure and Risk Assessment for Benzo(a)pyrene and Other Polycyclic Aromatic Hydrocarbons. Volume 2. Naphthalene

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An Exposure and Risk Assessment for Benzo[a]pyrene and Other Polycyclic Aromatic Hydrocarbons

Volume II. Naphthalene

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16. Abstract (Limit: 200 words)

This report assesses the risk of exposure to polycyclic aromatic hydrocarbons (PAHs). This is Volume II of a four-volume report, analyzing 16 PAHs; this volume concerns naphthalene. This study is part of a program to identify the sources of and evaluate exposure to 129 priority pollutants. The analysis is based on available information from government, industry, and technical publications assembled in June of 1981.

The assessment includes an identification of releases to the environment during production, use, or disposal of the substance. In addition, the fate of naphthalene in the environment is considered; ambient levels to which various populations of humans and aquatic life are exposed are reported. Exposure levels are estimated and available data on toxicity are presented and interpreted. Information concerning all of these topics is combined in an assessment of the risks of exposure to naphthalene for various subpopulations.

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AN EXPOSURE AND RISK ASSESSMENT FOR BENZO[a]PYRENE AND OTHER POLYCYCLIC AROMATIC HYDROCARBONS:

VOLUME II. NAPHTHALENE

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FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. Assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. The risk assessment process integrates health effects data (e.g., carcinogenicity, teratogenicity) with information on exposure. The components of exposure include an evaluation of the sources of the chemical, exposure pathways, ambient levels, and an identification of exposed populations including humans and aquatic life.

This assessment was performed as part of a program to determine the environmental risks associated with current use and disposal patterns for 65 chemicals and classes of chemicals (expanded to 129 "priority pollutants") named in the 1977 Clean Water Act. It includes an assessment of risk for humans and aquatic life and is intended to serve as a technical basis for developing the most appropriate and effective strategy for mitigating these risks.

This document is a contractors' final report. It has been extensively reviewed by the individual contractors and by the EPA at several stages of completion. Each chapter of the draft was reviewed by members of the authoring contractor's senior technical staff (e.g., toxicologists, environmental scientists) who had not previously been directly involved in the work. These individuals were selected by management to be the technical peers of the chapter authors. The chapters were comprehensively checked for uniformity in quality and content by the contractor's editorial team, which also was responsible for the production of the final report. The contractor's senior project management subsequently reviewed the final report in its entirety.

At EPA a senior staff member was responsible for guiding the contractors, reviewing the manuscripts, and soliciting comments, where appropriate, from related programs within EPA (e.g., Office of Toxic Substances, Research and Development, Air Programs, Solid and Hazardous Waste, etc.). A complete draft was summarized by the assigned EPA staff member and reviewed for technical and policy implications with the Office Director (formerly the Deputy Assistant Administrator) of Water Regulations and Standards. Subsequent revisions were included in the final report.

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AN EXPOSURE AND RISK ASSESSMENT FOR BENZO[a]PYRENE AND OTHER POLYCYCLIC AROMATIC HYDROCARBONS

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2.0 Technical Summary

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3.2 Fate and Distribution in the Environment
3.3 Effects and Exposure--Humans
3.4 Effects and Exposure--Aquatic Biota
3.5 Risk Considerations

VOLUME III Anthracene, Acenaphthene, Fluoranthene, Fluorene, Phenanthrene, and Pyrene

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4.1 Materials Balance
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The Materials Balance for Naphthalene (Section 3.1) was produced by Acurex Corporation, under Contract No. 68-01-6017 to the Monitoring and Data Support Division (MDSD), Office of Water Regulations and Standards (OWRS), U. S. Environmental Protection Agency. Patricia Cruse was the task manager for Acurex, Inc.; other contributors include Robert DeRosier, Kenneth Moss and Stephen Wendt. Patricia Leslie was responsible for report production on behalf of Acurex, Inc.

John Segna and Michael Slimak were the EPA project managers for this assignment.

1.0 INTRODUCTION

The Office of Water Regulations and Standards (OWRS), Monitoring and Data Support Division, of the U.S. Environmental Protection Agency is conducting a program to evaluate the exposure to and risk of 129 priority pollutants in the nation's environment. The risks to be evaluated include potential harm to human beings and deleterious effects on fish and other biota. The goals of the program under which this report has been prepared are to integrate information on cultural and environmental flows of specific priority pollutants, to estimate the likelihood of receptor exposure to these substances, and to evaluate the risk resulting from such exposures. The results are intended to serve as a basis for estimating the magnitude of the potential risk and developing a suitable regulatory strategy for reducing any such risk.

This report, comprised of four separate volumes, provides a summary of the available information concerning the releases, fate, distribution, effects, exposure, and potential risks of the 16 priority pollutants that are polycyclic aromatic hydrocarbons (PAHs). The chemical structures of these compounds are shown in Figure 1-1.

The number of chemicals considered in this exposure and risk assessment is appreciable. The possibility of preparing 16 separate exposure and risk assessment documents was considered and rejected because it would lead to considerable redundancy and because so little information was available on some of the individual PAHs. As an alternative, the 16 PAHs were organized at the onset of the work into three groups, as indicated in Figure 1-1.

The rationale for the organization into these three specific groups included considerations of materials balance, chemical properties related to fate and environmental pathways, and health effects, as described briefly below.

- Naphthalene is the only one of the 16 PAHs with substantial U.S. commercial production and with a significant potential for direct exposure to consumers of a commercial product (mothballs). It is significantly more volatile and more water soluble than any other PAH. It was not anticipated to have carcinogenic effects in humans.

- Anthracene, acenaphthene, fluorene, fluoranthene, phenanthrene and pyrene are all imported in rather small quantities for special commercial uses. These compounds are three- and four-ring PAHs, with moderately low volatility and water solubility. The question of their possible carcinogenicity was expected to require careful review. Most of the information pertaining to this group is specific to anthracene.

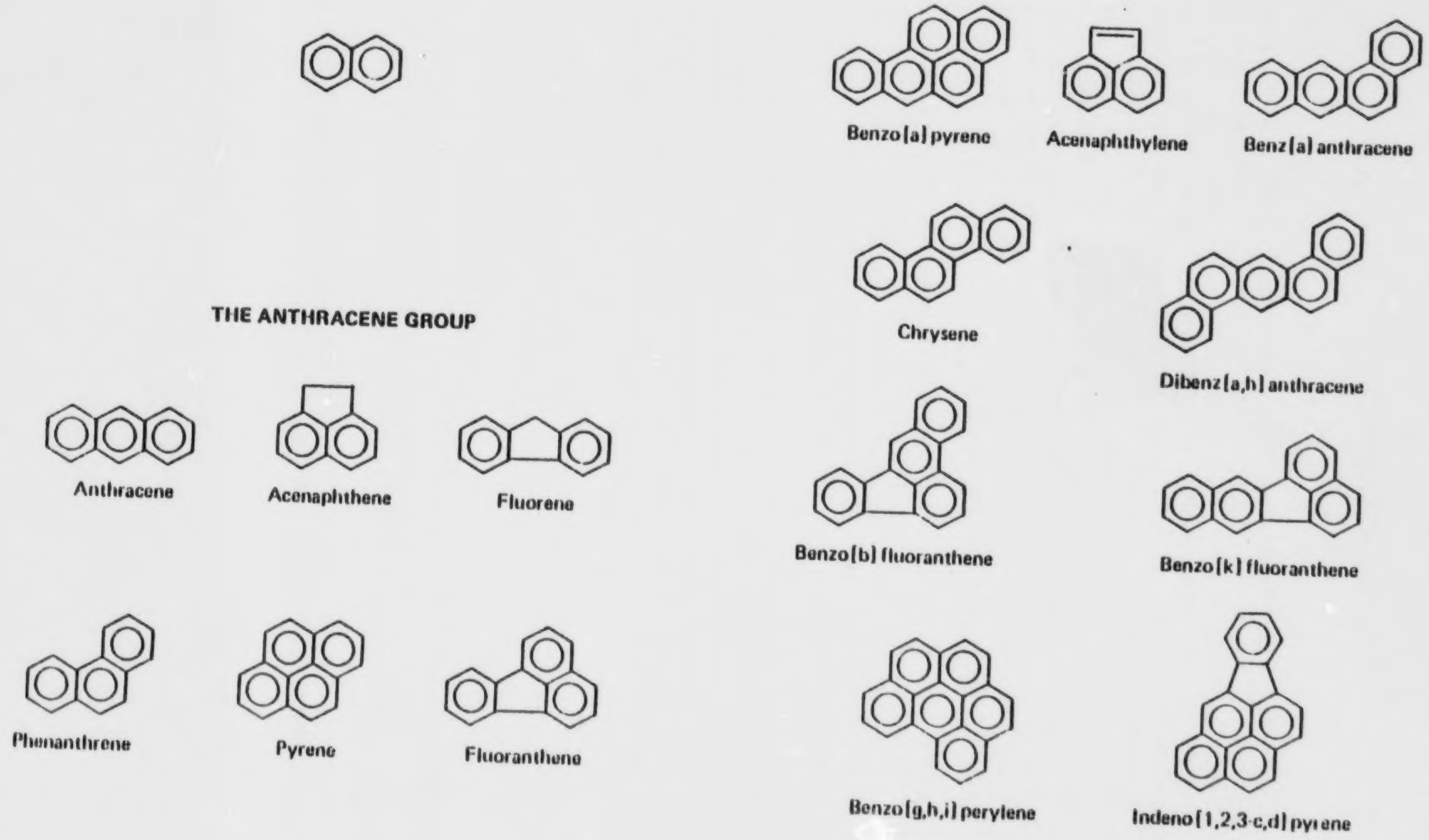

Benzo [a] pyrene
Acenaphthylene
Benz [a] anthracene
Chrysene
Dibenz [a,h] anthracene
THE ANTHRACENE GROUP
Anthracene
Acenaphthene
Fluorene
Benzo [b] fluoranthene
Benzo [k] fluoranthene
Phenanthrene
Pyrene
Fluoranthene
Benzo [g,h,i] perylene
Indeno [1,2,3-c,d] pyrene

FIGURE 1-1 STRUCTURES OF THE PRIORITY POLLUTANT POLYCYCLIC AROMATIC HYDROCARBONS

- Benzo[a]pyrene (BaP) and the eight other PAHs in the third group have no commercial production or use, except as research laboratory standards. They are released to the environment inadvertently by combustion sources. With one exception (acenaphthylene), the chemicals in this group have very low vapor pressures and water solubilities. Several of the PAHs in the BaP group had been identified as carcinogens. Much of the information regarding this group of compounds is for BaP.

The exposure and risk assessment for each of the three groups of PAHs was treated in a separate chapter of a multivolume report; Chapter 3.0 (Volume II) concerns naphthalene; Chapter 4.0 (Volume III) concerns the anthracene group PAHs; and Chapter 5.0 (Volume IV) concerns the benzo[a]pyrene group PAHs. These chapters are bound separately.

Potential waterborne routes of exposure are the primary focus of these exposure and risk assessments because of the emphasis of OWRS on aquatic and water-related pathways. Inhalation exposures are also considered, however, in order to place the water-related exposures into perspective. Each chapter contains major sections discussing the following topics:

- Information on environmental releases of the subject PAHs, including the form and amounts released and the receiving medium at the point of entry into the environment (materials balance);

- Description of the fate processes that transform and/or transport the compounds from the point of release through environmental media until exposure of humans and other receptors occurs, and a summary of reported concentrations detected in the environment, with a particular emphasis on aquatic media;

- Discussion of the available data concerning adverse health effects of the subject PAHs on humans, including (where known) the doses eliciting those effects and an assessment of the likely pathways and levels of human exposure;

- Review of available data concerning adverse effects on aquatic biota and the levels of environmental exposure; and

- Discussion of risk considerations for various subpopulations of humans and other biota.

Two comments regarding the materials balance section are appropriate. First, these sections were based in large part on draft material prepared by Acurex Corporation, under EPA Contract 68-01-6017, and provided to Arthur D. Little, Inc. by EPA. Second, the phrase "materials balance" is somewhat inappropriate when applied to chemicals such as the PAHs that are produced primarily as byproducts of combustion processes. Since most PAH production is inadvertent rather than deliberate commercial production, the conventional approach of trying to balance production versus use and environmental release is not strictly applicable to these chemicals. Therefore, the materials balance sections of these exposure and risk assessments are focused on estimates of releases from major sources such as combustion; considerable uncertainty is associated with most of these estimates.

After an initial review of the three exposure and risk assessments covering all 16 priority pollutant PAHs, it was determined that one chemical, benzo[a]pyrene, was of appreciably greater interest to OWRS than were the other 15 compounds studied. This interest reflects the more extensive data base available for assessment of environmental fate and exposure and also the existence of some, although limited, dose-response data to which various extrapolation models can be applied for estimation of potential human carcinogenic risk from ingestion of BaP. For the other PAHs considered, data on carcinogenic or other long-term effects were generally limited, nonquantitative, and/or did not indicate statistically positive results. Table 1-1 presents a summary of the hazard of the 16 priority pollutant PAHs in terms of carcinogenicity, based on qualitative review of available information.

For these reasons, the technical summary presented in Volume I is organized somewhat differently than the rest of the report (Chapter 3.0-5.0) (Volumes II-IV). The summary is focused on benzo[a]pyrene as the PAH of greatest interest. The estimated releases to the environment, environmental fate, monitoring data, human effects and exposure, biotic effects and exposure, and risk considerations concerning BaP are presented in expanded summary form. Abbreviated summaries are then provided for naphthalene, anthracene group PAHs, and the other PAHs considered.

Included in the summary volume are critical data and references to the literature so that this volume may be read and understood by itself without reference to the separately bound Chapters 3.0-5-0. The latter volumes contain more extensive compilations of data, more detailed discussions of the available information and of the interpretations drawn, and more complete documentation of the multiple literature sources that were reviewed in the course of this work.

TABLE 1-1. SUMMARY OF EVIDENCE FOR CARCINOGENICITY OF PRIORITY POLLUTANT PAHs

PAH*	Basis
Benzo[a]pyrene	Positive oral carcinogen with other positive carcinogenic data.
Dibenz[a,h]anthracene	Positive oral carcinogen with other positive carcinogenic data.
Benz[a]anthracene	Positive oral carcinogen with other positive carcinogenic data.
Benzo[g,h,i]perylene	Not tested orally, other positive carcinogenic or co-carcinogenic data.
Benzo[b]fluoranthene	Not tested orally, other positive carcinogenic or co-carcinogenic data.
Chrysene	Not tested orally, other positive carcinogenic or co-carcinogenic data.
Indeno[1,2,3-c,d]pyrene	Co-carcinogen or initiator with negative carcinogen or *in vivo* mutagen.
Pyrene	Co-carcinogen or initiator with negative carcinogen or *in vivo* mutagen.
Fluoranthene	Co-carcinogen or initiator with negative carcinogen or *in vivo* mutagen.
Benzo[k]fluoranthene	Negative in a single carcino genic study.
Phenanthrene	Several negative carcinogenic and mutagenic studies but not tested orally.

TABLE 1-1. SUMMARY OF EVIDENCE FOR CARCINOGENICTY OF PRIORITY POLLUTANT PAHs (Continued)

Anthracene	Negative studies, tested orally.
Naphthalene	Negative studies, tested orally.

[*] No data for evaluation of carcinogenicity were available for acenaphthene, acenaphthylene, or fluorene.

3.0 NAPHTHALENE

3.1 MATERIALS BALANCE

3.1.1 Introduction

One perspective from which exposure to a chemical may be evaluated is that of a materials balance. Since the total mass of all materials entering a system equals the total mass of all materials leaving that system, excluding those materials the system accumulates or retains, a materials balance may be performed around any individual operation that may ultimately place a specific population at risk (e.g., process water discharges creating groundwater contamination). Each overall materials balance, therefore, consists of a collection of smaller ones, each of which is directed to specific releases to the environment. It is beyond the scope of this section to predict the fate of the chemical following release.

This section reviews data concerning the production, use, and release of naphthalene within the United States. Information from the available literature has been compiled to present an overview of major sources of the environmental release of naphthalene. Annotated tables have been included to aid data evaluation.

A major source of naphthalene released to the environment is combustion. There are very few monitoring data, and the extent to which the reported emission factors are representative of the wide range of combustion conditions is unknown. The conventional approach of balancing production versus use and environmental release is not strictly applicable to napthalene since a major portion of the environmental load is inadvertently released from combustion sources. Therefore, the estimates reported within this Section should be regarded as indications of the relative magnitude of naphthalene releases to the environment and used to identify the most important sources.

Section 3.1.2 discusses the production of naphthalene and the releases due to production and inadvertant sources. The major uses of naphthalene, and the attendant environmental releases, are reviewed in section 3.1.3. Section 3.1.4 presents a discussion of the disposition of naphthalene discharged to municipal waste facilities, i.e., publicly owned treatment works (POTWs). A materials balance table for naphthalene and a summary of the major findings are presented in section 3.1.5.

3.1.2. Production

3.1.2.1 Overview

Naphthalene is produced by distillation of coal tar recovered from byproduct coking of coal and, to a lesser extent, is obtained from dealkylation of methyl naphthalene found in petroleum. In 1978, 165,000 kkg of naphthalene were recovered from coal tar; 70,290 kkg were obtained from petroleum (Abshire *et al.* 1980). Additionally 3,260 kkg of naphthalene were imported and 3,960 kkg were exported, resulting in an available U.S. supply of 234,590 kkg. Table 3-1 lists naphthalene producers, along with their locations and capacities.

TABLE 3-1. U.S. NAPHTHALENE PRODUCERS AND CAPACITIES, 1980 (10^4 kkg)[a]

Producer	Location	Capacity	Raw Material Used
Allied Chemical	Detroit, MI Ironton, OH	3.4[b]	Coal Tar
Ashland Oil	Ashland, KY	4.1[b]	Petroleum
Getty Oil	Delaware City, DE	4.5[b]	Petroleum
Koppers Co.	Cicero, IL Follansbee, WV	8.6[b,c]	Coal Tar
Monsanto	Chocolate Bayou, TX	4.1[c]	Petroleum (Ethylene By-product)
U.S. Steel	Clairton, PA Gary, IN	7.0[c]	Coal Tar
	Total	31.7	

a) SRI 1980.
b) Product is sold.
c) Product is captively consumed.

In order to recover naphthalene from coal tar, the crude tar is distilled and fractionated. The middle oil fraction containing most of the naphthalene and tar acids, is pumped into shallow pans and allowed to cool, crystallizing the naphthalene. The crystalline material is centrifuged and recovered as crude naphthalene. For a refined product, the crude naphthalene is distilled, washed, and sublimed.

Naphthalene is recovered from petroleum fractions containing large amounts of methyl naphthalenes by dealkylation in the presence of hydrogen at elevated pressure and temperature. Typical feedstocks include distilled bottoms from catalytic reformate or refraction cycle oils (Lowenheim and Moran 1975). Feeds are pumped to the dealkylation reactor. As the product exits the reactor, it is quenched and sent to a separator; effluents from the separator are distilled in order to recover naphthalene, gasoline and fuel oil. Petroleum-derived naphthalene is usually >99% pure and low in sulfur content.

3.1.2.2 Environmental Releases from Production

No specific data concerning environmental releases of naphthalene from production were found; however, an SRI study (Brown 1975) estimated that 0.0004% - 0.07% of the total naphthalene production is lost to the environment. Of that portion lost, 48% is estimated to be emitted to the atmosphere, 6% discharged to water, and 46% land disposed. Based upon an average production loss of 0.035%, a total of 83 kkg of naphthalene was estimated to be released to the environment from production by both coal tar and petroleum processes; of that amount, 40 kkg were emitted to the atmosphere, 5 kkg discharged to water and 38 kkg disposed of on land (see Table 3-2).

A comparison of coal tar and petroleum-based naphthalene recovery processes indicates that most of the 5 kkg of naphthalene discharged to water probably comes from coal tar facilities (Brown 1975). Major wastewater sources are extraction and wash tank effluents; specific flow rates and naphthalene concentrations were not found in the literature surveyed.

Land-disposed solid wastes consist of process sludge, discarded clay (from petroleum purification processes), spent catalysts, and on-site wastewater treatment sludge. Again, no specific data concerning quantities of these solids or their naphthalene concentrations were found.

3.1.2.3 Inadvertent Sources of Naphthalene

Although naphthalene itself is not used as a raw material in the wood preserving, paint, ink, or textile industries, it has been detected in wastewater streams from these industries (EPA 1980c). Since these industries utilize many naphthalene-containing products such as creosote, dyes, and surface-active agents, naphthalene present in such waste streams is probably due to degradation of these compounds.

Table 3-2. Estimated Environmental Releases of Naphthalene from Production and Inadvertent Sources, 1978 (kkg)

		Environmental Releases				
		Water		Land	Air	
Production	Quantity	Surface	POTW			Total
Coal Tar	165,000	5		38	40	83[a]
Petroleum	70,290					
Inadvertent Sources						
Wood Preserving[b]		<1	29			29
Textile Industry[c]		neg	<1	neg	NA	<1
Paint Formulation[d]		neg	<1	neg	NA	<1
Ink Formulation[e]		neg	<1	neg	NA	<1
Residential Coal Combustion[f]		neg		neg	1,000	1,000
Primary Residential Wood Heating[g]		neg		neg	2,000	2,000
Auxiliary Residential Wood Heating[g]		neg		neg	2,000	2,000
Cigarette Smoke[h]		neg		neg	2	2
Utility Industrial Internal Combustion Engines[i]		neg		neg	4	4
Gas-and Oil-Fired Residential Sources[j]		neg		neg	70	70
Coal Production and Distillation[k]		300	200	200	300	1,000
Oil Spills[l]		30		neg	NA	30

a) Based on Brown 1975 release estimates: see text.
b) See Appendix A, Note 2.
c) Based on total industry flow rate of 1.89×10^6 ℓ/day, 300 d/yr operation, and a median of 22 μg/ℓ in secondary effluent (EPA 1980c, EPA 1980d). Negligible is defined as <1 kkg. NA = not available.
d) Based on EPA, 1979g. 300 d/yr, 2.4 kg naphthalene discharged/day (total industry).
e) Based on EPA, 1979h. Mass loading of 0.001 kg/day industry wide, 300 d/yr operation; >90% of discharge is sent to POTWs.
f) Based on 0.15g naphthalene emitted/kg coal combusted (EPA 1977a) x $8,688 \times 10^3$ kkg coal consumed for residential combustion (DOE 1980).
g) Based on 0.25g naphthalene emitted/kg wood consumed (average for baffled and nonbaffled stoves EPA 1980a) and wood consumption of 6.9×10^6 kkg for primary heating and 9.2×10^6 kkg for auxiliary heating (EPA 1980a; Census 1979).
h) Based on 616×10^9 cigarettes produced (USDA 1979) x 3 μg naphthalene emitted/cigarette (Schmeltz et al. 1978).
i) EPA 1979a.
j) EPA 1979b.
k) Includes emissions from coke oven doors (air release) and 43 kkg (POTW release) from decanter tank tar sludge from spray cooling of coke oven gases (EPA 1980b). Based on 90,000 mg naphthalene/kg coal tar (Rhodes 1954; Lowry 1945) and discharge factors (kg/kkg coke of 0.00395 (ammonia liquor), 0.0115 (cooler blowdown), and 0.00341 (benzol plant) and coke production of 44.5×10^6 kkg (EPA 1977d; DOE 1979). Distribution: 33% direct, 25% POTW, 2% deep well injection, 40% quenching (20% land, 20% air) (EPA 1979c).
l) Based on 3.6×10^7 ℓ of various oils - crude (36%) diesel (18%) fuel (42%), waste (2%) lube (0.3%) and other (1.7%) spilled in navigable waters in 1978 (U.S. Coast Guard 1980) oil density of 0.85 and naphthalene content of 1,000 mg/kg in crude oil (Guerin 1978; Guerin et al. 1978, EPA 1979i).

On the basis of U.S. EPA Effluent Guidelines data concerning wood preserving plants, approximately 29 kkg of naphthalene are estimated to be discharged to POTWs per year; less than 1 kkg is discharged directly to water (EPA 1979d; see Appendix A, Note 1). Approximately 0.7 kkg and 0.003 kkg of naphthalene are discharged annually in raw wastewater from the paint and ink formulating industries, respectively (EPA 1979f,g; see Table 3-2). Discharges of naphthalene in textile mill effluents amount to 0.01 kkg per year (Table 3-2).

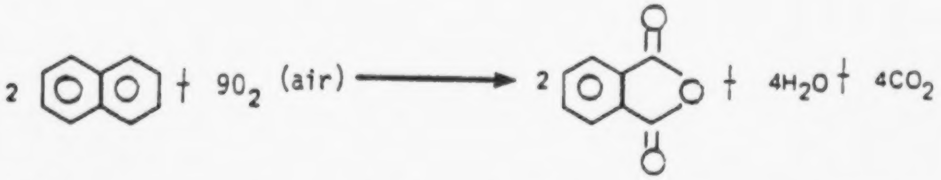
As is the case for all PAHs, naphthalene is released to the environment during combustion of fossil fuel, oil spills, and byproduct coking operations. Estimates of these releases are summarized in Table 3-2.

3.1.3 Uses

Table 3-3 summarizes the environmental releases estimated to occur as a result of the commercial use of naphthalene. Use in moth repellents accounts for the largest single release; this entire release is to the atmosphere. Phthalic anhydride production is the second largest source of naphthalene released to the environment during use.

3.1.3.1 Phthalic Anhydride

The manufacture of phthalic anhydride consumed 140,750 kkg of naphthalene in 1978 (Harris 1980, EPA 1973). Table 3-4 gives locations and naphthalene use capacities of the three domestic phthalic anhydride producers. Phthalic anhydride is obtained by oxidizing naphthalene in the vapor phase in the presence of a vanadium oxide catalyst (EPA 1977b).



Naphthalene conversion in the reactor is 100% (EPA 1976, Graham et al. 1962); therefore, the only atmospheric emission of naphthalene from the manufacture of phthalic anhydride stems from naphthalene storage facilities (EPA 1976). On the basis of an EPA emission factor of uncontrolled storage tank losses for naphthalene at phthalic anhydride plants (0.6 kg naphthalene/kkg phthalic anhydride produced) and assuming 4.5×10^5 kkg/yr phthalic anhydride produced, approximately 270 kkg of naphthalene were emitted to the atmosphere in 1978 (EPA 1976, USITC 1979). Emissions can be reduced 99% by using conservation vents on naphthalene storage tanks; for the most part, this technique is not employed (EPA 1976, EPA 1977b).

Table 3-3. Estimated Environmental Releases of Naphthalene from Use, 1978 (kkg)

Use	Quantity	Estimated Environmental Releases				
		Air	Land	Water		Total
				Surface	POTW	
Phthalic Anhydride[a]	140,750	270	neg	----neg----		270
Carbaryl Insecticide[b]	46,920	neg	neg	----neg----		neg
Beta-Naphthol[c]	18,770	neg	neg			neg
Synthetic Tanning Agents[d]	16,420	neg	neg	neg	2	2
Moth Repellents[e]	4,690	4,690	neg	----neg----		4,690
Surface Active Agents[f]	2,350	-----------neg-----------				neg
Miscellaneous Organic Chemicals[g]	4,690	------------47------------				47
Exports	3,960					
Total	238,550	4,980	16	neg	18	5,010

a) Negligible is defined as <1 kkg. Atmospheric emissions based on EPA emission factor of 0.60 (± 10%) kg naphthalene per kkg phthalic anhydride produced (EPA, 1976a) x 443,540 kkg PA produced in 1978 (USITC 1979).

b) Based on EPA (1972a/b) descriptions of waste treatment practices, see text.

c) Negligible release from production.

d) Based on Effluent Guidelines Division (EPA 1979h) wastewater data for leather tanning facilities; see Appendix A, Note 2.

e) Naphthalene volatilizes significantly at room temperature (Merck Index, 1976); all naphthalene used as a moth repellent is emitted to the atmosphere.

f) See Inadvertent Sources, Section 3.1.2.3.

g) See text.

TABLE 3-4. U.S. PHTHALIC PNHYDRIDE PRODUCERS AND LOCATIONS, AND CAPACITIES OF NAPHTHALENE USAGE

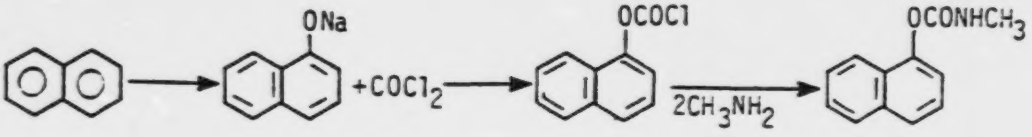
Company	Location	Nominal capacity, 10^3 kkg/yr	Raw Material	Process
Koppers Co.	Bridgeville, PA	40.8	Desulfurized Naphthalene	OWN(fluid bed)
Monsanto Co.	Bridgeport, NJ	40.8	Petroleum Naphthalene	Badger-Sherwin-Williams
US Steel	Neville Island, PA	68.0	Desulfurized Naphthalene	Badger-Sherwin-Williams
	Total	149.6		

Source: EPA 1977b.

If 100% of the naphthalene used in phthalic anhydride manufacture is converted to the desired product in the reactor and all water used is noncontact cooling water, very little, if any, naphthalene would be discharged in wastewater (EPA 1973, EPA 1976). Land-destined wastes, such as those arising from catalyst storage and disposal, contain no naphthalene (EPA 1976).

3.1.3.2 Carbaryl Insecticide

In 1978, approximately 46,920 kkg of naphthalene were consumed in carbaryl (Sevin®) insecticide manufacture. The reaction proceeds as follows:



Union Carbide, the only domestic producer, manufactures carbaryl at its facility in Institute, WV (EPA 1972a, Sittig 1977). Carbaryl is registered for use on about 70 crops and is used chiefly in the South and West.

The process wastes are primarily contained in liquid streams, vents, and a small amount of heavy residue. No specific naphthalene content of any waste stream was reported; waste treatment practices indicate, however, that the naphthalene loss from production of carbaryl insecticide is probably negligible. All aqueous wastes are sent to the plant's secondary waste treatment plant prior to direct discharge to a nearby river (EPA 1972a). Carbaryl levels in treated wastewater are relatively low, ranging from 0.01 mg/l to 1 mg/l (EPA 1972a); naphthalene concentrations should be even lower because the compound is converted to tetrahydronaphthalene (a manufacturing intermediate) with high yields. Atmospheric emissions of naphthalene are judged to be negligible since all toxic vents are flared at about 99% efficiency. The small quantities of solid residue generated are incinerated, also at about 99% efficiency; discarded containers are reportedly also burned.

The final product carbaryl, applied as a dust or liquid spray, contains no naphthalene (Kail 1980); therefore, no release to the environment occurs from its application. Apparently, naphthalene is not a degradation product or metabolite of carbaryl. Merck Index (1976) states that carbaryl is resistant to heat, light and acids, but hydrolyzes in the presence of alkalis. EPA (1972b) data show that carbaryl is not persistent in the environment; and in waters of pH 7.3 to 8.5, degradation was 95 to 100% complete in 3 to 7 days (EPA 1972b). The most likely degradation product (or metabolite) is 1-naphthol (EPA 1972c, Kail 1980); naphthalene is not found among identified mammalian urinary metabolites (EPA 1972c). Based on these data, use of carbaryl insecticide apparently is not a pathway for environmental release of naphthalene.

3.1.3.3 Synthetic Tanning Agents

Manufacture of synthetic tanning agents consumed 16,420 kkg of naphthalene in 1978; producers and their locations are listed in Table 3-5. Synthetic tanning agents, comprised mainly of 2-naphthalenesulfonic acid, its condensates, and salts, as well as small quantities of 1-naphthalenesulfonic acid, are utilized in both chrome and vegetable tanning. Naphthalene is released to the environment principally from wastewater streams; approximately 2 kkg per year are found in raw wastewater (EPA 1979h, see Appendix A, Note 2). Of the total 188 tanneries currently in operation in the U.S., 177 plants (90%) discharge to POTWs; 18 plants (10%) are direct dischargers (EPA 1979h). Approximately 88% of the indirect dischargers perform only coarse screening wastewater treatment, which is not efficient for naphthalene removal (EPA 1979h). The direct dischargers treat wastewater streams, for the most part, by activated sludge or aerated lagoons; naphthalene removal via these treatment methods is 69-100% efficient. On the basis of these treatment methods and efficiencies, approximately 1.8 kkg of naphthalene are believed to be discharged to POTWs from leather tanning; less than 0.1 kkg is discharged directly to surface water (EPA 1979h).

Atmospheric emissions of naphthalene from use of synthetic tanning agents are assumed to be negligible, as naphthalene itself is not introduced into the leather tanning facility. Naphthalene is found as a degradation product of 2-naphthalenesulfonic acid in wastewater streams and is possibly volatilized in aerated lagoons. On the basis of the total 2 kkg of naphthalene found in raw wastewater, the amount volatilized is assumed to be negligible.

Amounts of naphthalene in wastewater treatment sludge disposed of on land are also judged to be negligible. Although relatively large amounts of sludge are deposited on land annually from the leather tanning industry (203,000 kkg in 1974, EPA 1979h), no data concerning naphthalene content were found. These sludges are normally dewatered by evaporative lagoons and any naphthalene present would probably be volatilized.

3.1.3.4 Moth Repellent

Approximately 4,690 kkg of naphthalene (2% of the available U.S. supply) were utilized in moth repellents in 1978. Such use is decreasing due to the availability of para-dichlorobenzene (10,000 kkg of para-dichlorobenzene were utilized as moth repellent in 1978 [SRI 1979]) and the increased use of synthetic fibers. As noted later in Table 3-6, all of the naphthalene contained in moth repellent is emitted to the atmosphere. This estimate seems reasonable in that naphthalene volatilizes appreciably at room temperature (Merck Index 1976). Environmental releases from production of moth repellents are included in those for production of naphthalene because the compound is produced as a solid flake, powder or ball and simply repackaged as a consumer product; releases from handling processes are also included in the previously mentioned emission estimate for production.

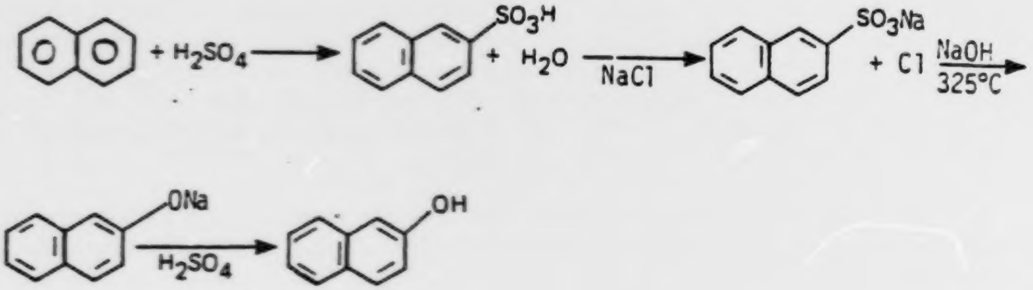
TABLE 3-5. PRODUCERS OF SYNTHETIC TANNING AGENTS AND THEIR LOCATIONS, 1978

Producer	Location
Ciba Geigy Dyestuff Division	Greensboro, NC
Diamond Shamrock	Carlstadt, NJ Cedartown, GA
Georgia Pacific Corp.	Bellingham, WA
Rohm and Haas	Philadelphia, PA

Source: Amos 1979.

3.1.3.5 β-Naphthol

Manufacture of β-naphthol consumed approximately 18,770 kkg of naphthalene in 1978, or about 8% of the available U.S. supply. Only one company, American Cyanamid, produces β-naphthol at its Willow Island, WV facility; plant capacity ranges from 15,800 to 18,100 kkg. Production requires reacting naphthalene with sulfuric acid and treating the sodium salt of the resultant 2-naphthalenesulfonic acid with sodium hydroxide (EPA 1977c) as shown below. The product is then distilled and sublimed.



No specific data were found concerning the environmental release of naphthalene from β-naphthol production. EPA (1977c) states that wastewater streams probably contain naphthols and naphthalenesulfonic acids; naphthalene itself was not listed. Washing and distilling the final product probably release small quantities (<1 kkg) of naphthalene to wastewater streams. Quantities of naphthalene released to the atmosphere and disposed of on land are unknown; however, process descriptions indicate that these releases are probably small (EPA 1977c).

β-naphthol is used in the manufacture of dyes and antioxidants for rubber. Releases of naphthalene from the use of these products could occur as the product decomposes. Such degradation is more likely to occur via oxidation than reduction; however, no specific data were found. Naphthalene is possibly formed when dye vats are cleaned by steam injection of solvents since steam hydrolysis forms naphthalene from β-naphthol. Environmental release from the use of β-naphthol-containing dyes from the paint and ink industries is considered under inadvertent sources, Section 3.1.2.3. Release of naphthalene from the use of antioxidants in rubber is assumed to be negligible, as the compound is tightly bound in the product.

3.1.3.6 Surface Active Agents

In 1978, production of surface active agents consumed 2,350 kkg of naphthalene, or about 1% of the available U.S. naphthalene supply. These compounds, used as dispersants and wetting agents in paint, dye, and paper-coating formulations, consist of 2-naphthalenesulfonic acid, its alkyl derivatives, and their salts. The compound 2-naphthalenesulfonic acid is manufactured by American Cyanamid in Marietta, OH (SRI 1980).

No specific data concerning environmental releases of naphthalene from 2-naphthalenesulfonic acid degradation were found. An EPA (1977c) study states that aqueous wastes streams contain sodium chloride and sulfate; however, naphthalene is not listed as present in this stream. Negligible (<1 kkg) discharge of naphthalene is probably a reasonable estimate in that byproduct 1-naphthalenesulfonic acid is hydrolyzed back to naphthalene, which is recovered by distillation (EPA 1977c). Quantities of naphthalene emitted to the atmosphere and disposed of on land are unknown, but are probably small.

Release of naphthalene from the use of surface active agents occurs indirectly, possibly from their degradation. Since 2-naphthalenesulfonic acid hydrolyzes to naphthalene in the presence of steam, the naphthalene detected in various studies of paint, textile, and ink discharge streams conducted by the U.S. EPA Effluent Guidelines Division is most likely a degradation product formed when vats and tanks are cleaned by steam injection (EPA 1979e,f). These industries use both surface-active agents and naphthalene-containing dyes; it is difficult to determine from which product the naphthalene arises. Therefore, these discharges are considered together under inadvertent sources, Section 3.1.2.3.

3.1.3.7 Miscellaneous Organic Chemicals

In 1978, approximately 4,690 kkg of naphthalene (about 2% of the available U.S. supply) were consumed in the manufacture of various organic chemicals, including α-naphthol, naphthaleneacetic acid, and decahydronaphthalene. As these compounds are each manufactured by three or fewer producers, the specific quantities produced are considered proprietary information. Uses of these chemicals are as dye intermediates, plant growth regulators, and solvents.

No specific data were found concerning quantities of naphthalene released to the environment from production or use of these compounds. Assuming a probable worst case scenario of a 1% loss during production, about 47 kkg of naphthalene would be released to the environment from manufacture of these compounds. Since naphthalene is converted into these products, naphthalene release from their use would occur only from degradation or impurities in the final product. Such releases are assumed to total less than 1 kkg.

3.1.4 Flow Through POTWs

Naphthalene loading to publicly owned treatment works (POTWs) is largely dependent upon the industries in the specific area. A framework for calculating a total naphthalene flow through the nation's POTWs is provided by data from a recent EPA study (EPA 1980e). A materials balance of naphthalene can be constructed by using a total nationwide POTW flow of 10^{11} l/day (EPA 1978) and median values of 6.5 μg/l (influent) and 0.2 μg/l (effluent). It is assumed for these calculations that influent and effluent flow rates are equal, i.e., that water losses from sludge removal and evaporation are small compared with influent flows. On the basis of these data, 237 kkg of naphthalene entered POTWs and effluents contained 7 kkg.

Quantities of naphthalene in sludge can be estimated from the amount of dry sludge generated annually, 6×10^6 kkg, and a naphthalene concentration of wet sludge equal to 242 μg/l (EPA 1980e). As wet sludge is 95% water by weight, approximately 29 kkg of naphthalene are discharged in sludge, which is assumed to be disposed of on land. Assuming that degradation of naphthalene within the POTW is negligible, the quantity of naphthalene volatilized, probably from aeration, is obtained by the difference between influent and effluent plus sludge values. Thus, a maximum of 200 kkg of naphthalene were emitted to the atmosphere from POTWs.

3.1.5 Summary

Table 3-6 summarizes the major environmental releases of naphthalene identified in this materials balance. The annual environmental release of naphthalene was estimated at approximately 11,500 kkg; over 90% was estimated to be due to atmospheric releases. Total releases to the different environmental compartments were estimated to be as follows: 10,600 kkg to air, 300 kkg to land, 340 kkg to surface waters, and 240 kkg to POTWs.

Production of naphthalene in 1978 totaled 235,290 kkg, 70% (165,000 kkg) of which was derived from coal tar and 30% (70,290 kkg) of which came from petroleum. Approximately 83 kkg of naphthalene were released to the environment from its production (by both processes). Of that total, 48% (40 kkg) was emitted to the atmosphere, 46% (38 kkg) was disposed of on land, and 6% (5 kkg) was discharged to water (Table 3-6).

Manufacture of phthalic anhydride, the largest single use of naphthalene, consumed 60% (140,750 kkg) of the available U.S. supply of the compound. Environmental releases of naphthalene from production of phthalic anhydride were approximately 270 kkg, all of which was emitted to the atmosphere. The remaining 40% (93,840 kkg) was utilized in the production of carbaryl insecticide, β-naphthol, synthetic tanning agents, surface active agents, and miscellaneous chemicals, and directly as a moth repellent. As shown in Table 3-6, the only appreciable environmental releases from the use of naphthalene are from its use as a moth repellent

TABLE 3-6. MATERIALS BALANCE: NAPHTHALENE, 1978 (kkg)

Source[a]		Estimated Environmental Releases				
		Air	Land	Water		
Production	Quantity			Surface	POTW	Total
Coal Tar	165,000	40	38	5		83
Petroleum	70,290					
Imports	3,260					
Exports	3,960					
Use						
Phthalic Anhydride	140,750	270	neg	----neg----		270
Carbaryl Insecticide	46,920	neg	neg	----neg----		neg
Beta-Naphthol	18,770	neg	neg	----neg----		neg
Synthetic Tanning Agents	16,420	neg	neg	neg	2	2
Moth Repellents	4,690	4,690	neg	----neg----		4,690
Surface Active Agents	2,350		-----------neg------------------			neg
Miscellaneous Organic Chemicals	4,690		------------47------------------			47
Inadvertent Sources						
Wood Preserving				<1	29	29
Textile Industry					<1	<1
Paint Formulation					<1	<1
Ink Formulation					<1	<1
Combustion		5100				5,100
Coal Tar Production/Distillation		300	200	300	200	1,000
Oil Spills				30		30
POTWs		200	29	7		240

a) See Tables 3-2 and 3-3 for specific sources.

(4,690 kkg) and in the production of phthalic anhydride (270 kkg), miscellaneous organic chemicals (47 kkg), and synthetic tanning agents (2 kkg); other uses are estimated to release negligible quantities (<1 kkg).

The wood preserving, paint, textile, and ink industries inadvertently release naphthalene to the environment, primarily to water. By far the largest discharge from these industries is 29 kkg (to POTWs) from the wood preserving industry; paint, ink, and textile industries each discharge less than 1 kkg to water. Approximately 5,100 kkg/yr of naphthalene are released to the atmospheric environment during combustion. The next largest inadvertent source of naphthalene releases is coal tar production and distillation, from which 1,000 kkg of naphthalene are released to the environment per year.

3.2 FATE AND DISTRIBUTION IN THE ENVIRONMENT

3.2.1 Introduction

This section characterizes the fate processes that determine the ultimate distribution of naphthalene in the aquatic environment and, therefore, the opportunities for waterborne exposure of humans and other biota. Section 3.2.2 presents an overview of the environmental loading of aquatic media with naphthalene, including releases directly to water and those resulting from physical transport (deposition from the atmosphere). In Section 3.2.3, physical/chemical properties of naphthalene are summarized in order to identify the processes that transform and transport the chemical upon its release to the environment (Section 3.2.3.1). Section 3.2.3.2 discusses the interplay of fate processes as it outlines the major pathways of naphthalene in aquatic environmental media. Modelling efforts were undertaken based upon environmental loadings estimated in Section 3.1 in order to characterize the fate and distribution of naphthalene in specific environmental scenarios; these are described in Section 3.2.3.3. Monitoring data from STORET and a limited number of other surveys are summarized in Section 3.2.4 to provide indications of the concentrations of naphthalene actually detected in aquatic environmental media. Finally, Section 3.2.5 summarizes those aspects of the fate and ultimate environmental distribution of naphthalene having the greatest significance for the waterborne exposure of humans and other biota.

3.2.2 Input to Aquatic Media

Data presented previously in Section 3.1 indicate that direct releases of naphthalene to surface water total an estimated 354 kkg each year. As shown in Table 3-7, about 85 percent of the total is associated with coal tar operations.

In addition to direct releases to surface water, naphthalene may be transported to the aquatic environment indirectly via wet and/or dry deposition of atmospheric releases. The air-to-surface pathway has been evaluated for naphthalene, and is detailed in Appendix B of this report. The results of that analysis are summarized in Table 3-8. Under ambient conditions in either rural or urban areas, atmospheric naphthalene will be almost entirely in the vapor phase with very little adsorbed to aerosols; even near combustion sources, only 2% of the naphthalene will be adsorbed. Since most naphthalene will be in the vapor phase, dry deposition is expected to be very slow (0.04-0.06 cm/sec). The vapor/aerosol partitioning also affects the precipitation scavenging ratio controlling wet deposition. The scavenging ratios estimated for naphthalene range from 53 under rural conditions to 2,500 for rainfall passing through the plume of a large combustion source.

Taking into account the observed concentrations of naphthalene, as well as the chemical degradation rates, it is estimated that only 2-3% of the emitted naphthalene will be deposited in either rural or urban areas; most of that deposition will be due to dry deposition processes.

TABLE 3-7. NAPHTHALENE RELEASES TO SURFACE WATERS (1978)[a]

Source	Release to Surface Water (kkg/yr)
Direct Releases	
Coal Tar Production and Distillation	300
Other Naphthalene Uses	∿12[c]
Oil Spills	30
POTWs	7
Naphthalene Production	5
Indirect Sources	
Atmospheric Deposition to Surface Waters[b]	∿5
Total	∿359

---

[a] Data from Section 3.1 Materials Balance.

[b] See following discussion of Atmospheric Deposition.

[c] 47 kkg release assumed to be divided equally among environmental compartments.

TABLE 3-8. AIR-TO-SURFACE PATHWAY EVALUATION FOR NAPHTHALENE[a]

	Rural	Urban	Near Combustion Source
Adsorbed Fraction Of Airborne Mass	7×10^{-6}	3×10^{-4}	2×10^{-2}
Dry Deposition Velocity (cm/Sec)	0.04	0.04	0.06
Precipitation Scavenging Ratio $\left[\frac{\text{ng/l (water)}}{\mu\text{g/m}^3\text{ (air)}}\right]$	53	71	2500
Percent of Atmospheric Emissions Deposited			
-dry deposition	2	2-3	
-wet deposition	<1	<1	
-total	2	2-3	

---

[a] These data are Arthur D. Little, Inc. estimates based on information in Appendix B and this chapter.

As shown in Table 3-9 the total amount of naphthalene emitted to the atmosphere of the United States in 1978 was approximately 10^4 kkg (Section 3.1). The data on deposition rates in Table 3-8 suggest that annual atmospheric deposition would be about 200 - 300 kkg. Some of the fallout will be directly deposited onto surface waters. If approximately 2% of the total area of the continental United States is surface water (U.S. Bureau of the Census 1980), direct deposition to aquatic systems would amount to approximately 5 kkg. Only a fraction of the remaining fallout, i.e., that deposited on land, would be transported to aquatic systems via surface runoff. There are insufficient data to permit an accurate estimation of the total input due to land-to-water pathways.

3.2.3 Environmental Fate

3.2.3.1 Basic Physical/Chemical Properties

Table 3-10 summarizes the physical and chemical properties of naphthalene that are relevant to its environmental fate and transport. The properties that have particular significance with respect to the partitioning of naphthalene among the environmental compartments are vapor pressure, water solubility, and octanol:water partition coefficient (K_{ow}). The K_{ow} provides a useful indication of the tendency for water-lipid and water-sediment partitioning, thereby enabling initial assessments of biodegradation, bioaccumulation, and sedimentation as fate processes. The Henry's law constant is simply the ratio of the vapor pressure at 25° C to the water solubility at the same temperature (without corrections for activity coefficients). This parameter is a good measure of the tendency for a solute to escape to the atmosphere from solution. The saturated concentration of naphthalene vapor in air was calculated from the Ideal Gas Law, and has been included in Table 3-10.

3.2.3.2 Pathways in the Aquatic Environment

Volatilization and Atmospheric Fate

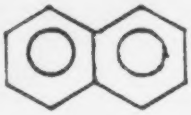
Naphthalene has the highest vapor pressure (4.9×10^{-2} torr) of the PAHs, a fact suggesting that volatilization may be more important for this compound than for the other PAHs. The actual rate of volatilization in a given setting is dependent upon temperature, wind velocity, and mixing rates of both air and water columns. In a stream 1.0 m in depth, naphthalene has been shown experimentally to have a half-life of 75 hours under conditions of a 0.1-m/sec current velocity and a 0.4-m/sec wind velocity. The rate of volatilization increased by a factor of 7.5 with a 10-fold increase in current velocity; the rate increased five times with a 10-fold increase in wind velocity. These variations are much more dramatic than the changes reported for the larger PAHs (Southworth 1979). These data are difficult to extrapolate to environmental systems since the temperature and rates of mixing will vary considerably with local water and weather conditions.

TABLE 3-9. ESTIMATED NAPHTHALENE RELEASES TO THE ATMOSPHERE (1978)

Source	Release to Atmosphere (kkg/yr)
Combustion (Primarily Residential Sources)	5075
Moth Repellant	4690
Coal Tar Production	300
Phthalic Anhydride Manufacture	270
POTWs	200
Naphthalene Production	40
Miscellaneous Organic Chemicals	~12
TOTAL	~10600

Source: Section 3.1

TABLE 3-10 BASIC PHYSICAL/CHEMICAL PROPERTIES OF NAPHTHALENE

Property		Reference
Structure:		
Formula:	$C_{10}H_8$	
MW:	128.19 g/mole	Hodgman (1961)
Melting Point (°C):	80.55	Hodgman (1961)
Boiling Point (°C):	217.9	Hodgman (1961)
Vapor Pressure (torr):	0.09 at 25°C	SRI (1980)
	0.22 at 25°C	calculated from data in Hodgman (1961)
	0.049 at 20°C	Callahan *et al*. (1979)
Water Solubility (mg/l):	31.7 at 25°C	SRI (1980)
	34.4 at 25°C	Callahan *et al.* (1979)
Log K_{ow}:	3.37	Callahan *et al*. (1979)
	3.29	SRI (1980)
Log K_{oc}:	3.03	SRI (1980)
Henry's Law: $\left(\frac{atm - m^3}{mol}\right)$:	4.8×10^{-4} at 25°C	calculated: $\frac{\text{vapor pressure}}{\text{water solubility}}$
Saturated Vapor Concentration (g/m^3):	0.62 at 25°C	calculated: PV=nRT

There is substantial evidence that, once released to the atmosphere, PAHs are readily degraded by photo-oxidation to produce oxygenated compounds, including quinone (Radding et al. 1976). No specific data on the rate of atmospheric photo-oxidation of naphthalene were encountered in the literature. However, the rate for oxidation of naphthalene by hydroxyl radicals in the atmosphere can be assumed to be intermediate between the 10 hours reported for larger PAHs (Radding et al. 1976; see also Volumes III and IV of this report) and the average of 45 hours estimated for benzene (Davis et al. 1977). To the extent that atmospheric naphthalene is adsorbed onto particulate materials, the rate of photo-oxidation may be lower than the half-life range of 10-45 hours would imply (Radding et al. 1976).

Adsorption and Sedimentation

Depending on the particulate content of the aquatic system, a significant fraction of the PAHs in the water column may be adsorbed onto suspended particulate material. Data on adsorption and concentration of three- and four-ring PAHs in the presence of various substrates such as activiated carbon, calcareous material, silica, glass, soil particles, and organic particles have been cited by numerous authors, and are summarized in Neff (1979) and in Volumes III and IV of this report. However, data referring specifically to naphthalene have not been encountered. The fact that the log octanol:water partition coefficient for naphthalene is 3.37 suggests that the extent of adsorption onto particulate may be lower than the 15-65% reported (Neff 1979) for anthracene (log K_{ow} = 4.45). The adsorption behavior of naphthalene probably depends upon the type of particulate material present, with stronger adsorption to organic than to mineral materials [by analogy to the behavior of anthracene (Volume III)].

Several authors (Smith et al.1978, Lewis 1975) have demonstrated that sorption of PAHs and other chemicals onto natural sediments and biogenous materials is a reversible equilibrium process. Again, the demonstrations relate specifically to higher molecular weight PAHs and not to naphthalene per se. However, because of naphthalene's relatively high water solubility and modest octanol:water partition coefficient the reversible adsorption/release process would be expected to be more important in maintaining a significant concentration of dissolved naphthalene in the water column. Zepp and Schlotzhauer (1979) have reported that naphthalene may exist primarily in the dissolved state in many inland water bodies and ocean waters.

Transport of the adsorbed naphthalene through the aquatic environment will be governed largely by the physical laws of sedimentation applicable to actual environmental conditions. The particulates gradually settle out of the water column; flocculation of suspended clay-sized particles (such as that which occurs in the increasing salinity gradient of an estuary) will increase the rate of deposition (Neff 1979).

In a study of a dispersion of Prudhoe Bay crude oil (Lee et al. 1978), naphthalenes were rapidly deposited in bottom sediments, while higher molecular weight PAHs accumulated more slowly. The authors suggested that accumulation by phytoplankton, which subsequently sink to the bottom, may be a significant means by which these relatively low molecular weight compounds are deposited in sediments.

Once deposited in sediment, PAHs in general, and presumably naphthalene in particular, are much less liable to be degraded photochemically and biologically. The concentration of naphthalene in sediment can be expected to be about two orders of magnitude higher than the concentration in solution (Lee and Anderson 1977), while higher molecular weight PAHs would show concentration ratios that were considerably higher. Sediment transport of naphthalene is probably qualitatively similar to pathways for other PAHs (see Volumes III and IV), with deltas and estuaries serving as a trap for riverborne particulate PAHs (White and Vanderslice 1980).

Chemical Degradation

The PAHs generally have high absorptivities for ultraviolet/visible light at wavelengths above the solar cut-off (300 nm). Direct photochemical degradation (initiated by absorption of light by the PAH compound, rather than by an intermediate photosensitizer) is expected to be a significant fate process for PAHs in water, in spite of the inefficient nature of photochemical reactions (quantum yields in the range of 0.001 to 0.01) (Andelman and Suess 1971; Smith et al. 1978; NAS 1972, Stevens and Algar 1968; Zepp and Schlotzhauer 1979). In contrast to the large PAHs, naphthalene has one of the highest photolysis quantum efficiencies (0.015), but about the lowest direct photolysis rate (half life = 71 hours) due to the lower sunlight absorption rates (the naphthalene absorption maxima coincide with the less intense solar radiation in the 280-320 nm range) (Zepp and Schlotzhauer 1979).

The role of photo-oxidation will vary with actual environmental conditions and the location of the compound in the water column. In turbid rivers, photolysis will be slowed by light attenuation and partitioning of the PAHs to sediments where no light is present. Figure 3-1 shows the relationship between depth and rate of direct photolysis for naphthalene during summer in aqueous (marine) environments. The data show photolysis half-lives for naphthalene of 53 days in mid-Gulf water and 2,000 days in the coastal environment. The mid-Gulf data refer to ocean water of low microbial and phytoplankton activity, while the coastal water data reflect the lower light penetration in the more biologically active environment. In each case, the rate for naphthalene photo-oxidation is two to three orders of magnitude lower than that for the higher molecular weight species, anthracene. The difference in the slope of the plot for naphthalene vs. that for anthracene results from the different absorption spectra of the two compounds and from the fact that the penetration of sunlight also varies with wavelength.

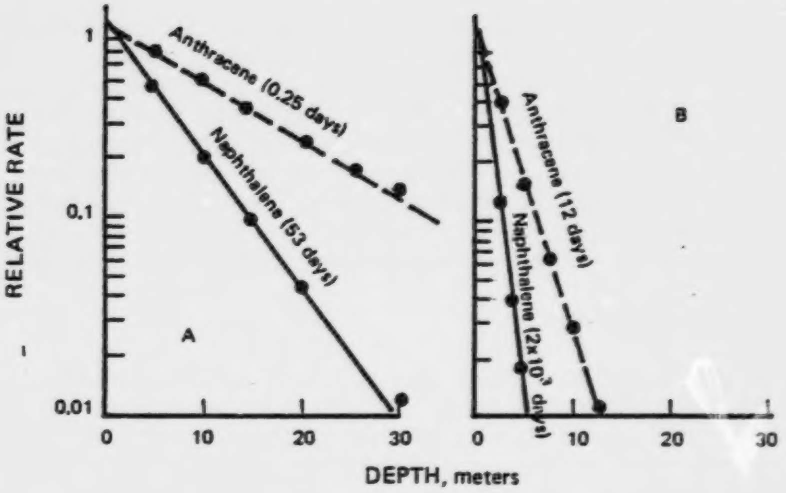
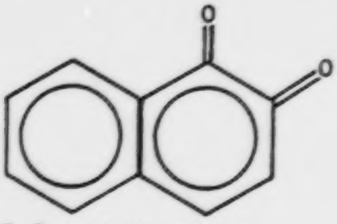


FIGURE 3-1 COMPUTED RELATIONSHIP BETWEEN DEPTH AND AVERAGE HALF-LIFE FOR PHOTOLYSIS OF NAPHTHALENE IN THE TOP 35 M OF SEAWATER.

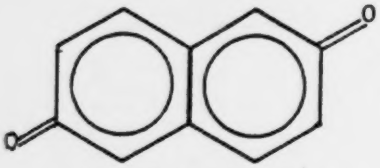
Note: Data for anthracene (dashed line) included for comparison. (A) mid-Gulf and (B) coastal water.

Source: Adapted from Zepp and Schlotzhauer (1979).

Zepp and Schlotzhauer (1979) calculated the half-lives for photo-oxidation of naphthalene in near surface waters (at 40°N latitude, mid-day, mid-summer) to be 71 hours for the direct process, and 10^9 hours for the photosensitized process. Thus, the quantum yield (efficiency) of the direct reaction ($Qr=0.015$) is 2×10^{10} times larger than that for sensitized photo-oxidation. Specific information on photo-degradation products of naphthalene was not encountered; napthoquinones such as those shown below are likely oxidation products.



1,2-naphthoquinone



2,6-naphthoquinone

In contrast to the above cited work are the results of Lee and Anderson (1977), which indicate that photolysis of naphthalene did not occur when the compound was added to a controlled ecosystem. These results are not necessarily directly applicable to the natural aquatic environment since other fate processes were affecting levels of naphthalene in the laboratory ecosystem.

The less important, slower oxidative reactions should also be mentioned in a discussion of the aquatic fate of PAHs. Radding et al. (1976) have summarized data on relative half-lives for oxidation of PAHs in aquatic environments by various agents: peroxide radicals ($RO_2\cdot$), singlet oxygen ($O\cdot$), ozone (O_3), chlorine (Cl_2) and hydroxyl radical ($OH\cdot$). Although naphthalene was not included in the study, the half-lives for other PAHs were generally >1,000 days for reaction with $RO_2\cdot$, 5 hours for reaction with $O\cdot$, <0.5 hours for reaction with Cl_2, and about 10 hours for reaction with $HO\cdot$. Reaction rates for naphthalene will probably be comparable to, or slower than, those for the higher molecular weight PAHs.

Possible reaction of naphthalene and other PAHs with chlorine (or ozone) in water or wastewater treatment plants is of interest as a possibly significant pathway within the cultural aquatic environment. During chlorination of biphenyl and naphthalene, Smith et al. (1978) identified several polychlorinated aromatics in addition to the quinones. Since many of these polychlorinated aromatics may be highly toxic and persistent, this pathway may be important as a potential source of new hazardous pollutants.

Biological Fate

Introduction

Biological processes such as uptake, depuration, and biodegradation are considered as pathways for naphthalene in aquatic systems. Overall, bioaccumulation of naphthalene is not significant in terms of reducing environmental concentrations of naphthalene, whereas neither microbial biotransformation nor biodegradation is considered the predominant fate mechanism for naphthalene in water.

Bioaccumulation

Bioaccumulation studies have been performed on both vertebrate and invertebrate species from freshwater and marine systems. In general, the results show rapid bioaccumulation but also a potential for depuration after exposure ceases.

Rainbow trout fingerlings (3-6 g) were exposed to naphthalene at concentrations of 0.023 or 0.005 mg/l for 8 hours, followed by a 24-hour elimination period. Naphthalene was readily accumulated in the 8 hours, but was also rapidly depurated with 4% of the tissue content remaining after 24 hours. Following a 6-week exposure to 0.017 mg/l, depuration took several hundred hours. Examination of the fish muscle tissue indicated that naphthalene itself broke down but its metabolites accumulated over the long term. The authors concluded that measurement of only the parent compound may give a false impression of rapid depuration of napthalene while its metabolites may be quite persistent (Melancon and Lech 1979).

Coho salmon and starry flounder were exposed to naphthalene at a concentration of 0.003 ± 0.002 mg/l. At five weeks, the point of maximum accumulation, the bioconcentration factor (BCF) was 80 for the salmon; the highest BCF measured in the flounder was 700 after one week of exposure (Table 3-11) (Roubal *et al*. 1978).

The benthic amphipod *Anonyx laticoxae* was exposed to naphthalene for periods from 4 to 27 days. Compared with levels in the surrounding environment (sediment or water), tissue bioconcentration factors were the least during sediment exposure (2-4), intermediate during static water exposure (10-50), and greatest in a flowing water system (1,000). The results of sediment exposure demonstrated relatively low bioavailability of naphthalene; the more significant routes of entry appeared to be via interstitial and water column exposure. During a constant exposure to 22 μg/l total naphthalenes, the amphipods reached a threshold of accumulation after 7 days; most of the uptake was of the alkylated forms of naphthalene (Anderson *et al*. 1979).

TABLE 3-11. BIOACCUMULATION OF NAPHTHALENE IN TWO FISH SPECIES[a]

Species	NAPHTHALENE ACCUMULATION							
	Weeks Of Exposure							
	2		3		5		6	
	BCF	mg/kg dry tissue	BCF	mg/kg dry tissue	BCF	mg/kg dry tissue	BCF	mg/kg dry tissue
Coho Salmon[b] (*Oncorhynchus kisutch*)	20	0.07 ± 0.03	50	0.14 ± 0.07	80	0.24 ± 0.06	40	0.12±0.06

Species	Weeks Of Exposure				Weeks Of Depuration			
	1		2		1		2	
	BCF	mg/kg dry tissue	BCF	mg/kg dry tissue	BCF	mg/kg dry tissue	BCF	mg/kg dry tissue
Starry Flounder (*P. stellatus*)	700	2.1 ± 1.5	240	0.72 ± 0.30	100	0.30 ± 0.02	270	0.80 ± 0.04

---

a) Flow-through exposure to 0.003 ± 0.002 mg/l.

b) Note that after 6 weeks of exposure and 1 week of depuration, no naphthalene was detected.

Source: Roubal *et al.* (1978)

Harris et al. (1977) reported a whole-body BCF of 5,000 (wet weight basis from dry weight data) in the saltwater species copepod (Eurytemora affinis) after 9 days of exposure. Lee et al. (1972) determined BCFs for three benthic marine fish in short-term studies (1-3 hours): sand goby (Gillichtus mirabilis) 63; sculpin (Oligocottus maculosus) 32; and sand dals (Citharichtys stigmaeus) 77.

Microbial Biotransformation

Naphthalene is one of the most commonly studied PAHs in regard to biodegradation. It is readily susceptible to microbial degradation; however, the rate and extent of degradation vary considerably depending upon environmental conditions. Influences on the rate include temperature, availability of other nutrients, and the microbial population, among others. Most studies have been conducted in simplified systems with the goal of eliciting biodegradation; actual environmental persistence may be longer than persistence measured in laboratory studies due to external factors that are controlled in the laboratory. This section describes the biodegradability of naphthalene based upon laboratory and field studies, including data on rate and metabolic pathways, with a discussion of the effect of important variables on the rate of reaction.

It is commonly thought, for several reasons, that microbial communities have had time to evolve the requisite enzyme systems for degradation of this class of organics, in contrast to some of the highly persistent synthetic organic compounds. Naphthalene, as well as other PAHs, is present naturally in many soils (Alexander 1977). It has been suggested that natural plant organics, such as diterpenes and sterols, may undergo reduction and aromatization to PAHs (McKenna and Heath 1976). Natural combustion sources (wildfire) may also introduce PAHs into the environment.

Since PAHs are commonly found in association, naphthalene is rarely found alone in the environment. There is evidence that co-metabolism of PAHs may occur in the presence of monocyclic aromatics; for example, naphthalene was more completely degraded in the presence of dodecane or benzene than it was alone (Walker and Colwell 1975). Most of the studies discussed in this section, however, concern direct biodegradation of naphthalene itself.

The metabolic pathway followed in the biodegradation of naphthalene is both compound- and species-dependent. In general, however, the two processes shown in Figure 3-2 are typical. Microbial (more specifically, bacterial) degradation is reported to occur through cis-dihydrodiol (Gibson 1976, 1977). Further oxidation leads to formation of catechols, which are subsequently subject to further ring fission. There is evidence that yeasts, molds, and fungi (Cunninghamella bainierri) may oxidize naphthalene by the mono-oxygenase-induced mechanism reported for mammmals (Gibson 1977). This process forms reactive arene oxides, which isomerize to phenols or undergo enzymatic hydration to yield trans-dihydrodiols.

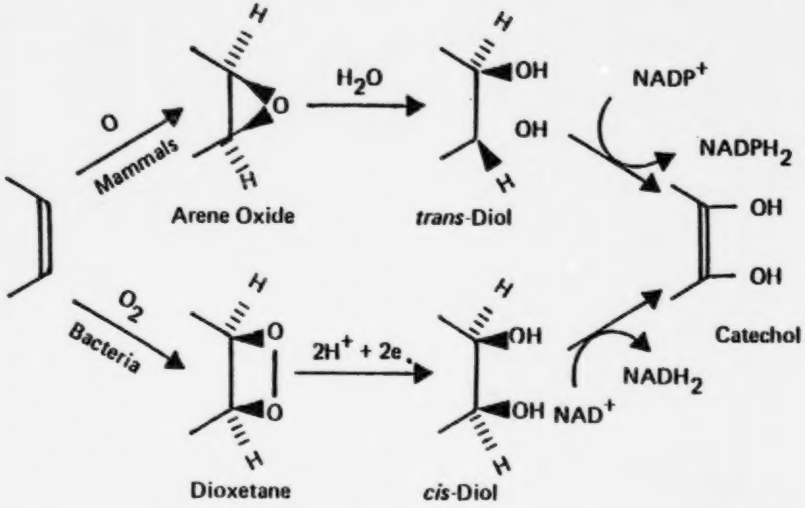

O
Mammals
O_2
Bacteria
H
O
Arene Oxide
Dioxetane
H_2O
$2H^+ + 2e$
OH
trans-Diol
cis-Diol
$NADP^+$
$NADPH_2$
NAD^+
$NADH_2$
Catechol

FIGURE 3-2 PATHWAYS UTILIZED BY MAMMALS AND BACTERIA FOR THE OXIDATION OF AROMATIC HYDROCARBONS

Source: Gibson (1976).

Table 3-12 presents a number of reaction products reported to result from the biodegradation of naphthalene. For the most part, they are intermediates in the multistep pathway of reactions leading ultimately to complete mineralization of naphthalene into its inorganic constituents.

The rate of biodegradation of naphthalene is quite variable. Table 3-13 presents quantified rates of biodegradation reported for naphthalene in soil and freshwater systems. Due to the variation in test methods, analytical techniques, microbial species, and data analyses used in biodegradation testing (i.e., a lack of a standard procedure), the results from the different tests reported in Table 3-13 cannot be compared directly.

The turnover time and transformation rates in Table 3-14 in both acclimated and unacclimated stream populations (Schwall and Herbes 1978) provide an estimate of naphthalene's environmental persistence and illustrate the effect of microbial adaptation on the overall rate. The turnover time was 7.1 hours in acclimated populations and 125 days in nonacclimated populations. Based upon other laboratory studies, the 7.1-hour acclimated turnover time seems quite slow. Other processes, such as adsorption and deposition into inaccessible bottom sediments, may have affected the removal of naphthalene from solution before significant biodegradation could take place. The extent to which these rates are applicable to other aquatic systems is unknown because of the scarcity of field data.

Because biodegradation may be a significant fate pathway for naphthalene, it is worthwhile to briefly review the environmental factors influencing biodegradation. The fission of aromatic rings usually requires the addition of oxygen, most often from O_2 (Alexander 1977), a fact implying that PAH biodegradation can take place only under aerobic conditions. In the absence of O_2, it has been hypothesized that the presence of nitrate, which is rapidly reduced, may supply oxygen that can be used in degradation (Alexander 1977). The assimilation of hydrocarbons by sulfate-reducing bacteria is thought to occur primarily with aliphatics and not aromatics, although several bacterial strains have been isolated in the laboratory that can utilize aromatic hydrocarbons (Haas and Applegate 1975).

The pH of the soil solution also influences degradation rates. A pH increase from 4.5 to 7.4 approximately doubled the rate of breakdown of PAHs (Verstraete et al. 1976). Whether this increase was due to population changes or to direct impact on the chemical reaction was not explored.

Natural humic polymers may act as stabilizing agents on aromatics and reduce their biodegradability (Pitter 1976). In addition, adsorption, which is an important process for insoluble compounds like PAHs, may reduce microbial access to these substances. However, since the organic fraction of the sediment would eventually be subject to microbial breakdown in the course of the system's carbon cycling, any adsorbed naphthalene

TABLE 3-12. BACTERIAL BIODEGRADATION PRODUCTS REPORTED FOR NAPHTHALENE

Degradation Product	Reference
1-naphthol; 4-hydroxyl-1-tetralone; trans-1,2-dihydroxyl-1,2-dihydronaphthalene; 2-naphthol; 1,2- and 1,4-naphthoquinone	Cerniglia _et_ _al_. (1979)
cis-dihydrodiols	Cerniglia _et_ _al_. (1979)
1,2-dihydroxynaphthalene, salicylaldehyde, salicylate, catechol	Colwell and Sayler (1978)

TABLE 3-13. BIODEGRADATION RATES OF NAPHTHALENE

Test Type/Population Origin	Compound Tested	Results	Source
$^{14}CO_2$ evolution from stream sediment populations from petroleum contaminated area	^{14}C-naphthalene	90% of total PAH transformed at 40 hours; rate = 0.14 hr	Schwall and Herbes (1978)
Warburg O_2 consumption, non-acclimated sludge population	Naphthalene	33-64% of TOD[a] transformed	Malaney *et al.* (1967)
Shake flask freshwater sediment population	Hydrocarbon mixture (parraffines, mono- and dicyclic hydrocarbons)	Naphthalene: 3-12% decrease together with dodecane: 25-35% decrease (1% sterile hydrocarbon; 28 days)	Walker and Colwell (1975)
$^{14}CO_2$ evolution with seawater population from treated area	Naphthalene	0.4 µg/l/day (by day 3)	Lee *et al*, (1978)

[a] Theoretical Oxygen Demand

TABLE 3-14. KINETIC PARAMETERS OF NAPHTHALENE TRANSFORMATION IN OIL-CONTAMINATED STREAM AND UNCONTAMINATED STREAM SEDIMENT SAMPLES

Compound	Rate Constant k (1/h)		Turnover Time[a]		Transformation Rate (μg/g per h)[b]	
	Contaminated	Uncontaminated	Contaminated	Uncontaminated	Contaminated	Uncontaminated
Naphthalene	1.4×10^{-1}	$<4 \times 10^{-4}$	7.1 hours	125 days	1.0	$<8 \times 10^{-6}$

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[a] Turnover time = 1/k

[b] Transformation rate = k x concentration.

Source: Schwall and Herbes (1978).

would in time be subject to biodegradation. Adsorption onto organic matter may also increase biodegradation by retaining the substrate in areas with dense and active microbial populations, which tend to be concentrated on organic particulates. The fate of naphthalene adsorbed onto inorganic sediment is unknown; however, it would probably be more persistent than that on organic sediment.

Thus, naphthalene is one of the most readily biodegradable PAHs. However, an initial period of acclimation by the degrading population is usually required. Reported half-lives for microbial degradation are on the order of 1 to 2 days in laboratory studies with acclimated populations.

3.2.3.3 Modeling of Environmental Distribution

Introduction

Very limited monitoring data are available to describe the extent of naphthalene contamination in the environment. Of the 16 PAHs, naphthalene has the highest water solubility, and is released to the environment at a higher rate than the others, suggesting that waterborne exposure to naphthalene would be higher than to other PAHs. Several modeling efforts were undertaken in order to estimate the distribution of naphthalene among the environmental compartments, and to describe the important aspects of the behavior of naphthalene in selected environmental settings. The Mackay equilibrium model was used to predict the partitioning of naphthalene among environmental compartments in equilibrium. The Exposure Analysis Modeling System (EXAMS), developed by the U.S. EPA, was used to study the fate of naphthalene in generalized aquatic environments.

Mackay Equilibrium Partitioning Model

As an initial step in hazard or risk assessments for toxic chemicals and as an aid in the interpretation of monitoring data, a preliminary estimate of a pollutant's environmental distribution can often be made by inspection of the chemical's properties. A simple approach to approximating the environmental partitioning has recently been proposed by Mackay (1979) based upon the fact that in a system at equilibrium, the fugacity of the pollutant must be the same in all phases.

In Mackay's Level I Model, all environmental compartments (phases) are assumed to be directly or indirectly connected and at equilibrium. The compartments considered are air, water, suspended solids in water, sediment, and aquatic biota. The Level I calculations require that these compartments be described roughly (volumes, temperature, biota "concentration", etc.), and the model output will clearly depend upon the nature of the "environment" selected. The selected compartments are shown schematically in Figure 3-3. The figure is not drawn to scale, although compartment size and density, where appropriate, have been indicated. The temperature was assumed to be 25°C.

A relatively small number of chemical-specific parameters is required to calculate equilibrium partitioning; these are presented in Table 3-15. For an absolute estimate of the equilibrium concentrations in each phase, it is necessary to estimate the total amount of the chemical that is likely to be in the selected environment. (Note that the predicted concentration ratios between the phases will not be affected by the value selected.) For these calculations, the total amount of naphthalene in the system was 22.5 kg. Details of the model calculation methods are provided elsewhere (Mackay 1979) and are not repeated here.

The results obtained for naphthalene are presented in Table 3-16. Naphthalene undergoes considerable volatilization upon standing, as one might expect from its relatively high vapor pressure. The Mackay model predicts that at equilibrium 77.8% of the environmental naphthalene will reside in the air compartment. The different fractions of material in the suspended solids and sediments are a result of the different sizes of the compartments in the model; concentrations in each of these compartments are essentially the same. Within the water column, most of the naphthalene is estimated to be in solution; suspended solids and biota contain only a small percentage of the total water column quantity. The water concentrations are lower than concentrations in the solid phases by a factor of 20.

EXAMS Model

The U.S. EPA Athens Environmental Research Laboratory has developed an interactive system designated as EXAMS (Exposure Analysis Modeling System) to carry out exposure analyses for organic chemicals in six freshwater environments (Smith et al. 1978, U.S. EPA 1980c). In performing these analyses, the model assumes "steady-state" behavior and considers the fate and transport of the organic chemical as it passes through a system composed of one or more water and sediment compartments. Within the aqueous compartments, biota (fish, algae) may be assumed to exist and the extent of bioconcentration of the organic chemical in the species may be calculated.

Using the precompiled environments, plus chemical-specific input parameters, EXAMS models the bulk transport of a chemical within aqueous compartments (mixing, dilution, transport downstream), as well as the processes of volatilization (loss to the atmosphere), adsorption onto sediments and suspended solids (by physical forces or ion exchange), hydrolysis (assumed first-order reaction), photolysis (assumed first-order reaction), biodegradation, and dissociation (for organic acids, bases, complexes).

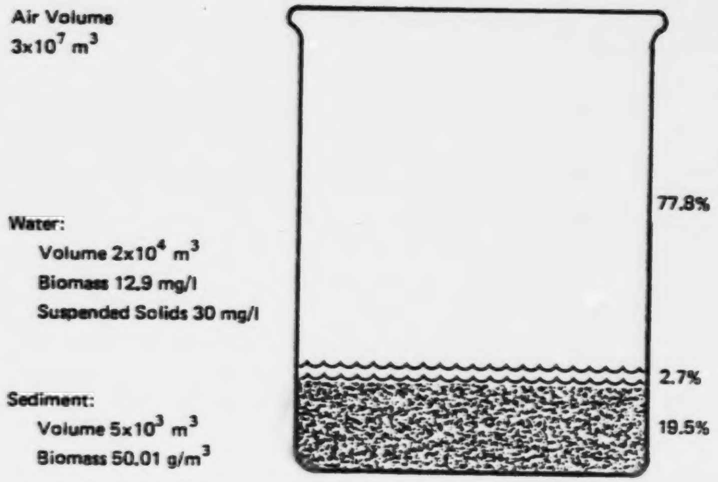
Air Volume
3×10^7 m^3
77.8%
Water:
Volume 2×10^4 m^3
Biomass 12.9 mg/l
Suspended Solids 30 mg/l
2.7%
Sediment:
Volume 5×10^3 m^3
Biomass 50.01 g/m^3
19.5%

FIGURE 3-3 MACKAY ENVIRONMENTAL MODEL SYSTEMS AND PREDICTED DISTRIBUTION OF NAPHTHALENE

TABLE 3-15. VALUES OF PARAMETERS USED FOR CALCULATING THE EQUILIBRIUM DISTRIBUTION OF NAPHTHALENE PREDICTED BY THE MACKAY FUGACITY MODEL

Chemical - Specific Parameters (25°C)	
Henry's Law Constant (m^3-atm/mole)	4.8×10^{-4}
Adsorption Coefficients:	
Suspended Solids ($0.01 \times K_{oc}$)	21.43
Sediment ($0.01 \times K_{oc}$)	21.43
Biota ($0.2 \times K_{ow}$)	468.9
Total Amount in System (kg)	22.5(175 moles)
Compartment - Specific Parameters (25°C)	
Air:	
area	$1 \times 10^4 m^2$
depth	$3 \times 10^3 m$
volume	$3 \times 10^7 m^3$
Water:	
area	$1 \times 10^4 m^2$
depth	2m
volume	$2 \times 10^4 m^3$
biomass content	12.9 mg/l
suspended sediment	30 mg/l
Sediment:	
area	$1 \times 10^4 m^2$
depth	$5 \times 10^{-1} m$
volume	$5 \times 10^3 m^3$
biomass content	$50.01 g/m^3$
wet sediment density	$1.85 g/cm^3$
sediment dry weight = (100 x wet weight)/137	

TABLE 3-16. EQUILIBRIUM PARTITIONING OF NAPHTHALENE CALCULATED USING THE MACKAY FUGACITY MODEL

	Partitioning At Equilibirum		
Compartment	Moles	Concentration	Percent
Air	136.7	0.583 mg/m^3	77.8
Water	4.7	0.33 mg/l	2.7
Suspended Solids	0.003	0.65 mg/kg	0.0017
Sediment	34.3	0.65 mg/kg	19.53
Aquatic Biota	0.03	14.24 mg/kg	0.0163
Sediment Biota	0.003	14.24 mg/kg	0.0016
TOTAL IN SYSTEM	175		

EXAMS was run for naphthalene. All six EXAMS environments (pond, eutrophic lake, oligotrophic lake, river, coastal plain river and turbid river) were modelled, using the ecosystem parameters that are provided with the model. The values entered for the chemical-specific parameters are given in Table 3-17. Any input variables not in the table were set to zero; the physical processes associated with these other variables (such as hydrolysis) either were not considered important for naphthalene or were calculated by the model using the basic input data.

The loading rate used for the EXAMS calculations was estimated from data presented in the materials balance section of this chapter (3.1). The largest continuous discharge of naphthalene to surface waters arises from coal tar production activities; a much smaller discharge is estimated to occur when the coal tar is used to produce naphthalene. Appendix A of Volume IV of this report lists coke-oven tar production sites in 19 states, with production by state ranging from 26% to 0.5% of the total production. Assuming that there is one site per state, and that the release of naphthalene is proportional to the production level at each site, the annual release at each site can be expected to range from 78 kkg/yr to 1.5 kkg/yr (i.e., 26% to 0.5% of the 300 kkg/yr discharged from coal tar production and distillation reported in Table 3-7). Assuming plant operation of 300 day/yr, the daily load by state would range from 260 kg/day to 5 kg/day. Since it is possible that there may be more than one site per state, the lower loading rate was considered a more appropriate approximation of the actual discharges to environmental waters. Therefore, a discharge rate of 0.2 kg/hr (4.8 kg/day) was used in the model.

One scenario that could result in short-term discharges at considerably higher levels than the level chosen for use in the EXAMS calculation is spillage or leakage of petroleum [crude oil has a naphthalene content of 1,000 mg/kg (see Section 3.1)]. There are insufficient data to estimate either the amount of naphthalene released to the aquatic environment in such an incident, or the behavior of the naphthalene released in crude oil. Partitioning among the compartments and removal processes could be different from those characteristic of low-level, continuous discharges used in the model since equilibrium may not be achieved.

When the calculated concentration of naphthalene is below the maximum solubility level, maximum concentrations and accumulations will be proportional to the loading and can be adjusted accordingly, without affecting the self-purification times and percentage distribution of naphthalene. Table 3-18 summarizes the naphthalene concentrations predicted by EXAMS for the simulated environments under steady-state conditions. Water concentrations in the relatively static pond and lake systems were approximately 0.005 mg/l to 0.48 mg/l; concentrations in the river systems were considerably lower, 1.9×10^{-4} mg/l to 1.7×10^{-3} mg/l, due to dilution and physical transport mechanisms. These aqueous concentrations are

TABLE 3-17. INPUT PARAMETERS FOR EXAMS MODELING OF THE FATE OF NAPTHALENE IN GENERALIZED AQUATIC SYSTEMS

Explanation	Input Value	References
Molecular wt. (g/mole)	128.1	Weast (1970)
Ratio of volatilization to reaeration rate	0.460	SRI (1980)
Aqueous solubility (mg/l)	31.7	May *et al*. (1978)
Partition coefficient biomass:water	322.0	SRI (1980)
Henry's Law Constant (atm m^3 $mole^{-1}$)	4.8×10^{-4}	Table 3-10
Partition coefficient octanol:water	2344	Callahan *et al*. (1979)
Second-order bacterial degradation rate constant (in water and in sediment) (ml/cell/hr)	1×10^{-7}	SRI (1980)
Increase in bacterial degradation rate per 10°C in temperature	2	SRI (1980)
Photolysis rate constant	9.76×10^{-3}	Calculated from data in Zepp and Schlotzhauer (1979)
Reference latitude for photolysis rate constant	35.00	Zepp and Schlotzhauer (1979)
Loading rate (kg/hr)	0.2	Data in Section 3.1

TABLE 3-18. STEADY-STATE CONCENTRATIONS OF NAPHTHALENE IN VARIOUS GENERALIZED AQUATIC SYSTEMS RESULTING FROM CONTINUOUS DISCHARGE AT A RATE OF 0.2 kg/hour[a]

		Maximum Concentrations							
System	Loading Rate (kg/hr)	Dissolved Water (mg/L)	Total Water (mg/L)	Pore Water (mg/L)	Sediment Deposits (mg/kg)	Plankton (μg/g)	Benthos (μg/g)	Total Steady-State Accumulation (kg)	Total Daily Load (kg/day)
Pond	0.2	0.48	0.48	0.4	58	154	128	5.0	4.8
Eutrophic Lake	0.2	5.4×10^{-3}	5.6×10^{-3}	1.4×10^{-3}	0.084	1.76	0.46	2.6	4.8
Oligotrophic Lake	0.2	2.6×10^{-2}	2.6×10^{-2}	1.9×10^{-3}	0.118	8.2	0.62	58	4.8
River	0.2	2.0×10^{-4}	2.0×10^{-4}	4.2×10^{-5}	0.004	0.06	0.01	0.22	4.8
Turbid River	0.2	1.9×10^{-4}	2.0×10^{-4}	7.4×10^{-5}	0.002	0.06	0.02	0.2	4.8
Coastal Plain River	0.2	1.7×10^{-3}	1.7×10^{-3}	4.2×10^{-4}	0.086	0.56	0.12	2.4	4.8

---

[a] All data simulated by EXAMS (U.S. EPA-SERL, Athens, Ga.) model.[See text for further information about input parameters and Smith et al. (1978) for a description of the model.]

well below the 31.7 mg/l solubility of naphthalene; therefore, these results may be extrapolated for larger discharges, providing steady-state conditions are reached.

Sediment concentrations ranged from 0.002 mg/kg in the turbid river system to 58 mg/kg in the pond. The high levels in the pond sediment result from the fact that removal processes, such as volatilization and physical transport, were too slow to compete with adsorption and sedimentation. The pond also contains a large amount of biota that are subject to sedimentation; the concentrations in biota are generally two to three orders of magnitude above levels in water.

Table 3-19 presents the EXAMS results concerning the fate of naphthalene in the aquatic systems. The distribution shown indicates the importance of the environmental conditions in the partitioning of naphthalene between water and sediments. The pond has significant sediment/water mixing and a large amount of suspended sediment and biota; adsorption and sedimentation is facilitated in this system, accounting for the observation that 80.54% of the naphthalene will be residing in the sediment. In contrast, the oligotrophic lake has more transport across system boundaries than the pond, and has very little suspended matter; consequently only 1.8% of the naphthalene will be in the sediment of this system. Furthermore, the lake contains more biota of the type that are not available for sedimentation, and fewer plankton than the pond, causing transport of naphthalene to lake sediment to be a slower process.

In the more dynamic systems, such as the rivers, transport beyond the model boundaries of the system accounts for most of the removal of naphthalene. Biological transformation is also important in the coastal plain river, which contains a significant amount of biota. Volatilization is particularly important as a removal process in the oligotrophic lake and the pond; chemical transformation (photolysis) is also significant in the clear oligotrophic lake, where light penetration is high; and biological transformation competes with volatilization in the pond. The fate of naphthalene in eutrophic lakes is governed primarily by biological transformation.

Based upon the distribution and fate data, and the input parameters for the various removal and degradation processes, the persistance of naphthalene can be estimated for each of the aquatic systems. These data are presented in Table 3-20. More than one-half of the accumulated load is removed from the river systems (physical transport) and the eutrophic lake system (biodegradation) within half a day. In contrast, EXAMS predicts that within 12 days of the cessation of discharge, only 28% of the naphthalene will be removed from the pond system (volatilization, chemical and biological degradation) and 56% will be removed from the oligotrophic lake system.

TABLE 3-19. THE FATE OF NAPHTHALENE IN VARIOUS GENERALIZED AQUATIC SYSTEMS[a]

System	Residing in Water at Steady-State	Residing in Sediment at Steady-State	Transformed by Chemical Processes	Transformed by Biological Processes	Volatilized	Lost by Other Processes[b]	Time System Self-Purification[c]
Pond	19.46	80.54	7.02	35.61	50.99	6.38	233.5 days
Eutrophic lake	86.41	13.59	0.45	95.87	3.65	0.03	35.2 days
Oligotrophic lake	98.20	1.80	39.12	0.33	56.77	3.78	58.56 days
River	78.06	21.94	0.06	3.08	1.11	95.75	15.1 days
Turbid River	86.26	13.74	0.05	3.05	1.10	95.81	6.5 days
Coastal Plain River	54.55	45.45	0.41	23.88	8.60	67.11	58.8 days

---

[a] All data simulated by the EXAMS (U.S. EPA-SERL, Athens Ga.) model. [See text for further information about input parameters and Smith *et al.* (1978) for a description of the model.]

[b] Including loss through physical transport beyond system boundaries.

[c] Estimate for removal of ca. 97% of the toxicant accumulated in system (5 apparent system half-lives). Estimated from the results of the half-lives for the toxicant in bottom sediment and water columns, with overall cleansing time weighted according to the pollutant's initial distribution.

TABLE 3-20. THE PERSISTENCE OF NAPHTHALENE IN VARIOUS GENERALIZED AQUATIC SYSTEMS AFTER CESSATION OF LOADING AT 0.2 kg/hour[a]

System	Time Period (days)	% Lost from Water	% Lost from Sediment	% Lost from Total System
Pond	12	90.85	13.55	28.59
Eutrophic Lake	0.5	62.53	0.70	54.13
Oligotrophic Lake	12	56.94	7.17	56.04
River	0.5	99.98	2.51	78.59
Turbid River	0.5	99.98	3.71	86.76
Coastal Plain River	0.5	92.93	1.34	51.30

---

[a] All data simulated by the EXAMS (U.S. EPA-SERL, Athens, Ga.) model. [See text for further information about input parameters and Smith et al. (1978) for a description of the model.]

Comparison of Mackay and EXAMS Predictions

The pond environment was chosen as the most appropriate EXAMS system to compare with the Mackay model since a pond has the least amount of transport across system boundaries. In spite of the fact that the Mackay water system was sized to correspond to the EXAMS pond, the two models are not directly comparable since other assumptions of each model are often quite different. The Mackay model includes the air compartment, whereas EXAMS models only the aquatic system. Furthermore, the Mackay model is simply a partitioning model; EXAMS utilizes kinetic data and includes processes that may occur after the chemical has been partitioned into one of the aquatic compartments. The concentration data predicted by the Mackay model are calculated from the amount of the chemcial partitioned to each compartment and the size of the compartments. Since these parameters are arbitrarily set, the raw concentration data cannot necessarily be taken as indicative of actual environmental concentrations, and the relative partitioning among the compartments is the most valuable result.

Table 3-21 summarizes some of the relevant data from the two models. The total load for the Mackay model was chosen so that the amount partitioned to water and sediment would be equal to the EXAMS pond accumulation. The actual concentrations predicted by the Mackay model are lower than the EXAMS data. However, the ratios of the concentrations predicted for the various compartments by the two models are fairly consistent. The ratios of the percentages of naphthalene expected to be dissolved or adsorbed are also in agreement. Note that 77.8% of the initial load to the Mackay system was partitioned to the atmosphere due to the large Henry's Law Constant for naphthalene.

3.2.4 Monitoring Data

3.2.4.1 STORET Data

Introduction

Monitoring data from the STORET Water Quality Information System (U.S. EPA 1980a and 1981) indicate limited sampling of naphthalene in ambient and effluent waters since 1978. Sampling activities have not been uniformly distributed across the country, representing only the geographic areas of the East (excluding New England), the South, and the West. Naphthalene concentrations for ambient and effluent waters, sediment, and fish tissue were recorded in the STORET system.

STORET monitoring data for naphthalene include observations for 26 states and the U.S. territory of Puerto Rico. Roughly 490 monitoring stations have recorded information; the following discussion is of ambient data registered as of November 20, 1980.

TABLE 3-21. COMPARISON OF RESULTS FROM MACKAY'S EQUILIBRIUM MODEL AND EXAMS FOR NAPHTHALENE IN A POND SYSTEM

EXAMS Results (Pond, 4.8 kg/day loading 5.0 steady-state accumulation)		Mackay's Results (22.5 kg in system)	
	Maximum Concentrations		Concentrations
Water	0.48 mg/l	Water	0.03 mg/l
Aquatic Biota	154 mg/kg	Water Biota	0.65 mg/kg
Sediment Biota	128 mg/kg	Sediment Biota	0.65 mg/kg
Sediment	58 mg/kg	Sediment	0.65 mg/kg
Accumulation		Percent of Chemical per Compartment[a]	
% in Water	19.46	% in Water	2.7%
% in Sediment	80.54	% in Sediment	19.5%

---

[a] 77.8% of the initial load was partitioned to the atmosphere.

Ambient and Effluent Waters

Roughly 302 ambient observations of naphthalene are stored in the STORET system; 96% of these observations are remarked. The remarked observations are reported as the detection limits used in sampling, and range up to 20 μg/l for naphthalene. A limit of 10 μg/l is recorded most frequently, i.e., for 52% of all samples analyzed. Table 3-22 presents the percentage distribution of ambient concentrations for naphthalene. Of the 294 remarked concentrations, 17% are no higher than 1 μg/l, 70% are between 1.1 and 10 μg/l, and 13 % are between 10.1 and 100 μg/l. The eight unremarked concentrations range from 0.005 μg/l to 17 μg/l. The state locations of these observations are also shown in Table 3-22.

Eighty-seven percent of the 534 effluent concentrations recorded as of April 9, 1981 (from 271 monitoring stations) are remarked. Table 3-22 shows the percentage distribution of effluent concentrations, remarked and unremarked, for naphthalene. Thirty-six percent of the 466 remarked concentrations are less than or equal to 1 μg/l, 60% between 1.1 and 10 μg/l, and 2% between 10.1 and 100 μg/l. Of 68 unremarked effluent concentrations, 12% are no higher than 1 μg/l, 22% between 1.1 and 10 μg/l; 50% are between 10.1 and 100 μg/l; 9% are between 100.1 and 1000 μg/l; and 7% are over 1000 μg/l. Three of the five observations over 1000 μg/l were recorded from sampling at a disposal site in Washington State; the fourth was from a textile plant effluent in South Bronx, New York; and the fifth from a chemical plant effluent in Kentucky.

Sediment

Eighty-four percent of the 130 observations for naphthalene in sediment (ambient waters) are remarked. The detection limits range up to 10,000 μg/kg, with 2,000 and 2,500 μg/kg accounting for 38% of the remarked observations.

Twenty-one unremarked observations indicate naphthalene concentrations in sediment ranging from 0.02 μg/kg to 496 μg/kg. The percentage distribution of observed concentrations of naphthalene in sediment is shown in Table 3-23.

Fish Tissue

All observations of naphthalene in fish tissue are remarked. Of the 73 remarked observations in STORET, 14% of the detection limits are no higher than 1 mg/kg; 86% are between 1.1 and 10 mg/kg (Table 3-23).

TABLE 3-22. DISTRIBUTION OF AMBIENT AND EFFLUENT CONCENTRATIONS (µg/l) FOR NAPHTHALENE - STORET 1980

AMBIENT DATA

TOTAL	NUMBER IN REMARKED CONCENTRATION RANGES					TOTAL	NUMBER IN UNREMARKED CONCENTRATION RANGES				
	≤1	1.1-10	10.1-100	100.1-1000	>1000		≤1	1.1-10	10.1-100	100.1-1000	>1000
294	50	206	38	--	--	8	6	1	1	--	--

Location of Unremarked Concentrations

Washington State: 0.06, 0.11, and 0.2 µg/l
Oregon: 0.005 µg/l
Pennsylvania: 0.24 and 1.4 µg/l
New York: 0.6 µg/l
North Carolina: 17 µg/l

EFFLUENT DATA

TOTAL	NUMBER IN REMARKED CONCENTRATION RANGES					TOTAL	NUMBER IN UNREMARKED CONCENTRATION RANGES				
	≤1	1.1-10	10.1-100	100.1-1000	>1000		≤1	1.1-10	10.1-100	100.1-1000	>1000
466	177	280	9	--	--	68	8	15	34	6	5

Location of Unremarked Concentrations >1000 µg/l:

Washington State: 6300, 9800, and 36000 µg/l (Queen City Disposal Site)
New York: 1030 µg/l (Plant Effluent - Textile)
Kentucky: 1300 µg/l (Treatment Plant Effluent - Chemical)

Source: STORET data as of April 9, 1981.

TABLE 3-23. DISTRIBUTION OF NAPHTHALENE CONCENTRATIONS IN SEDIMENT AND FISH TISSUE IN AMBIENT WATERS--STORET 1980

	TOTAL NO.	NUMBER OF OBSERVATIONS IN CONCENTRATION RANGES				
		≤1	1.1-10	10.1-100	100.1-1000	>1000
Sediment (μg/kg):						
Remarked	108	25	1	2	12	68
Unremarked	21	4	3	11	3	--
Fish Tissue (mg/kg):						
Remarked	73	10	63			
Unremarked	0					

Source: STORET data as of November 20, 1980.

3.2.4.2 Other Data Sources

Drinking Water

According to the U.S. EPA criteria document for naphthalene (U.S. EPA 1980b), naphthalene has been detected in drinking water supplies at concentrations up to 1.4 μg/l, in ambient water at up to 2.0 μg/l, and in sewage plant effluents at up to 22 μg/l. Levins et al. (1980) found no detectable levels of naphthalene in tap water samples from drainage basins in Cincinnati, St. Louis, Atlanta, and Hartford. Average concentrations found in raw wastewaters from the four municipal areas were:

2.1 μg/l from residential areas
2.6 μg/l from commercial areas
50.7 μg/l from light industrial areas
11.6 μg/l at POTW influent.

Effluents

Rawlings and DeAngelis (1976) have shown the range of naphthalene in textile effluents to be 0.003-300 μg/l. Other levels of naphthalene in industrial effluents have been reported by the U.S. EPA (1980b); the maximum industrial effluent concentration was 32,000 μg/l. Naphthalene concentrations in final effluents from industrial sewage were measured at a maximum level of 22 ug/l. Neither the location nor the type of industry was reported for these data.

Air

Various investigators have measured both the vapor and particulate levels of naphthalene in air. Krstulovic et al (1977) reported particulate levels of naphthalene for three Rhode Island cities corresponding to urban, suburban, and rural areas. These levels were 0.25 ng/m^3, 0.03 ng/m^3, and 0.003 ng/m^3, as presented in Table 3-24. Table 3-24 also includes data for air levels of naphthalene in samples taken at industrial sources. Bjorseth et al. (1978a,b) reported naphthalene vapor levels ranging from 11-1,100 μg/m^3 for vapor, and 0.09-4.0 μg/m^3 for particulate matter. The U.S. EPA has reported a measurement of 0.50 ng/m^3 of naphthalene in urban air; this concentration is an average of reported levels (U.S. EPA 1980b).

3.2.5 Summary - Ultimate Fate and Distribution

Most of the environmental releases of naphthalene are to the atmosphere. Atmospheric deposition (wet and/or dry fallout) is expected to remove only 2-3% (200-300 kkg on the basis of 1978 data) of the total atmospheric load. It is estimated that the amount deposited directly onto U.S. inland surface waters will be proportional to their area, i.e., 2% of the total continental United States. Therefore, ~5 kkg can be expected to fall on inland surface waters of the U.S. annually; only a fraction of the fallout to land will

TABLE 3-24. REPORTED LEVELS OF NAPHTHALENE IN AIR

Area Investigated	Concentration (ng/m^3)			Reference
	Vapor Level	Particulate Level	Total	
Atmosphere of coke plant[a]	$1.1 \times 10^4 - 1.1 \times 10^6$	$0 - 4.4 \times 10^3$		Bjorseth *et al.* (1978a)
Atmosphere of aluminum reduction plant[b]	$7.2 \times 10^2 - 3.1 \times 10^5$	$90 - 4 \times 10^3$		Bjorseth *et al.* (1978b)
Providence, R.I.[c]	0.1	0.25	0.35	Krstulovic *et al.* (1977)
Kingston, R.I.[c]	0.03	0.03	0.06	Krstulovic *et al.* (1977)
Naragansett Bay, R.I.[c]	0.05	0.003	0.053	Krstulovic *et al.* (1977)

[a] Range includes measurements for fall and spring sampling, using mobile, stationary, and personal sampling techniques.

[b] Ranges are for measurements using stationary and personal sampling techniques.

[c] Samples collected in September 1975: 9-hour collection time, northwest wind.

ultimately reach aquatic systems via runoff and leaching. The naphthalene remaining in the atmosphere is expected to undergo rapid photo-oxidation to quinones and other oxygenated compounds; however, a thorough review of the atmospheric fate pathways is beyond the scope of this report.

Since naphthalene has a vapor pressure of 0.09 torr at 25°C, and log of the octanol:water partition coefficient of 3.37, a large amount of the naphthalene in surface waters can be expected to be removed to the atmosphere via volatilization; removal to the sediment via adsorption and sedimentation may be important if there is a significant amount of suspended material in the aquatic system. Biodegradation may also be a significant fate process for naphthalene in aquatic systems. The application of the Mackay equilibrium partitioning model (Mackay 1979) confirms the prediction that large amounts of the environmental naphthalene will be in the atmosphere (78%) and sediment (20%). Calculations based on the Exposure Analysis Modeling System [EXAMS] also predict that biotransformation, volatilization, photolysis, and physical transport could all be important fate processes, depending upon the actual conditions in the environment. In comparison with the other PAHs, photolysis, oxidation, and sedimentation of napthalene are less important pathways; volatilization is the most important fate process in static aquatic systems. The extent of volatilization depends upon temperature, wind velocity, and current velocity. In rivers, the major fate pathway is transport of adsorbed naphthalene to the oceans.

EXAMS results for six generalized aquatic systems suggest that the naphthalene in sediment will tend to remain there unless there is considerable mixing between the sediment and the water column, since neither photolysis nor anaerobic degradation are important fate pathways. In summary, although the sediments and the water columns of aquatic systems may contain naphthalene, accumulation will occur in the sediment.

Monitoring data confirm that concentrations in sediment are higher than those in water. The STORET data base reports actual measurements of naphthalene in ambient waters ranging from 0.005 μg/l-17 μg/l; effluent concentrations up to 36,000 μg/l are reported. Actual sediment concentrations reported in STORET range from 0.02 μg/kg to 496 μg/kg. Drinking water concentrations up to 1.4 μg/l were reported in the literature. Ambient air concentrations of naphthalene were reported to be 0.35 ng/m^3 in an urban area, and 0.05 ng/m^3 in a rural area. Concentrations to which industrial workers may be exposed range from 10^2 ng/m^3 to 10^6 ng/m^3 in the vapor phase, and up to 4 x 10^3 ng/m^3 adsorbed onto particulate matter.

Some of the major sources of aquatic naphthalene, the predicted distribution, and the major fate processes are shown in Figure 3-4. There are very few experiments examining rates of degradation and removal specifically for naphthalene; most of the half-lives are estimated from measurements for the larger PAHs.

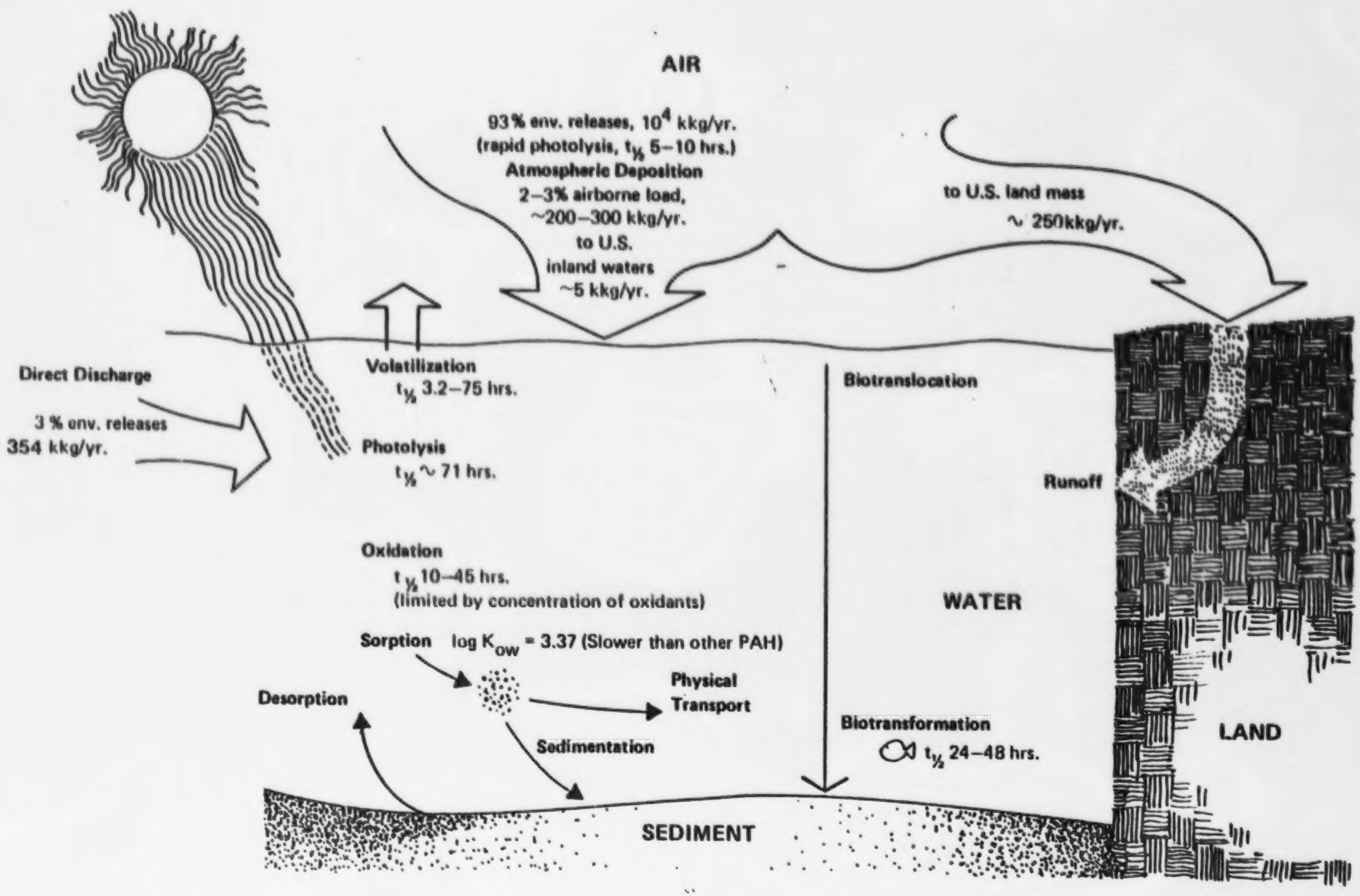
AIR
93% env. releases, 10^4 kkg/yr.
(rapid photolysis, $t_{1/2}$ 5–10 hrs.)
Atmospheric Deposition
2–3% airborne load,
~200–300 kkg/yr.
to U.S.
inland waters
~5 kkg/yr.
to U.S. land mass
~ 250kkg/yr.
Direct Discharge
3 % env. releases
354 kkg/yr.
Volatilization
$t_{1/2}$ 3.2–75 hrs.
Photolysis
$t_{1/2}$ ~ 71 hrs.
Oxidation
$t_{1/2}$ 10–45 hrs.
(limited by concentration of oxidants)
Sorption
log K_{ow} = 3.37 (Slower than other PAH)
Desorption
Physical Transport
Sedimentation
Biotranslocation
WATER
Runoff
Biotransformation
$t_{1/2}$ 24–48 hrs.
LAND
SEDIMENT

FIGURE 3-4 SOURCES AND FATE OF NAPHTHALENE IN THE AQUATIC ENVIRONMENT

3.3 EFFECTS AND EXPOSURE--HUMANS

3.3.1 Human Effects

3.3.1.1 Introduction

This section of the report summarizes the pertinent health effects associated with naphthalene exposure. The U.S. EPA (1980a) concluded that there were few or no quantitative data concerning the chronic toxicity or carcinogenicity of naphthalene from which to derive a water quality criterion for drinking water. Based on the apparent low levels of naphthalene in natural waters, they concluded that it did not appear that significant adverse effects would result from ingestion of water containing these low levels of naphthalene.

3.3.1.2 Pharmacokinetics

Naphthalene appears to be absorbed via all routes of exposure--ingestion, inhalation, and skin contact. The rate and extent of absorption by any route have not been studied in detail; however, numerous case reports of toxicity following ingestion or inhalation indicate appreciable absorption by these routes. One report by Dawson et al. (1958) suggests that skin absorption of naphthalene vapors occurred in infants when the skin was covered with baby oil. As is discussed below, newborn infants may be highly sensitive to naphthalene exposure.

The tissue distribution of naphthalene following absorption has apparently not been studied in detail; one study in ducks (Lawler et al. 1978), along with consideration of the high lipid solubility of naphthalene, suggests that naphthalene has a wide tissue distribution.

The metabolism of naphthalene has been extensively studied. The major pathways that have been elucidated are given in Figure 3-5. Presumably, these pathways are similar among human and other mammalian species. Of importance is the metabolism of naphthalene to toxic metabolites including 1- and 2-naphthol, 1,2-dihydroxynaphthalene and 1,2-naphthoquinone. Though the importance of the liver in the metabolism of naphthalene is clearly established, the involvement of other tissues has apparently not been studied with the exception of the metabolism in the eye.

3.3.1.3 Human and Animal Studies

Carcinogenicity

Results of the few studies on naphthalene carcinogenicity via oral or subcutaneous routes do not indicate a carcinogenic response (Table 3-25). Two experiments by Knake (1956) indicated a nonstatistically significant increase in lymphosarcomas in rats (subcutaneous injection) and of lymphocytic leukemia in mice (skin painting). These experiments, however,

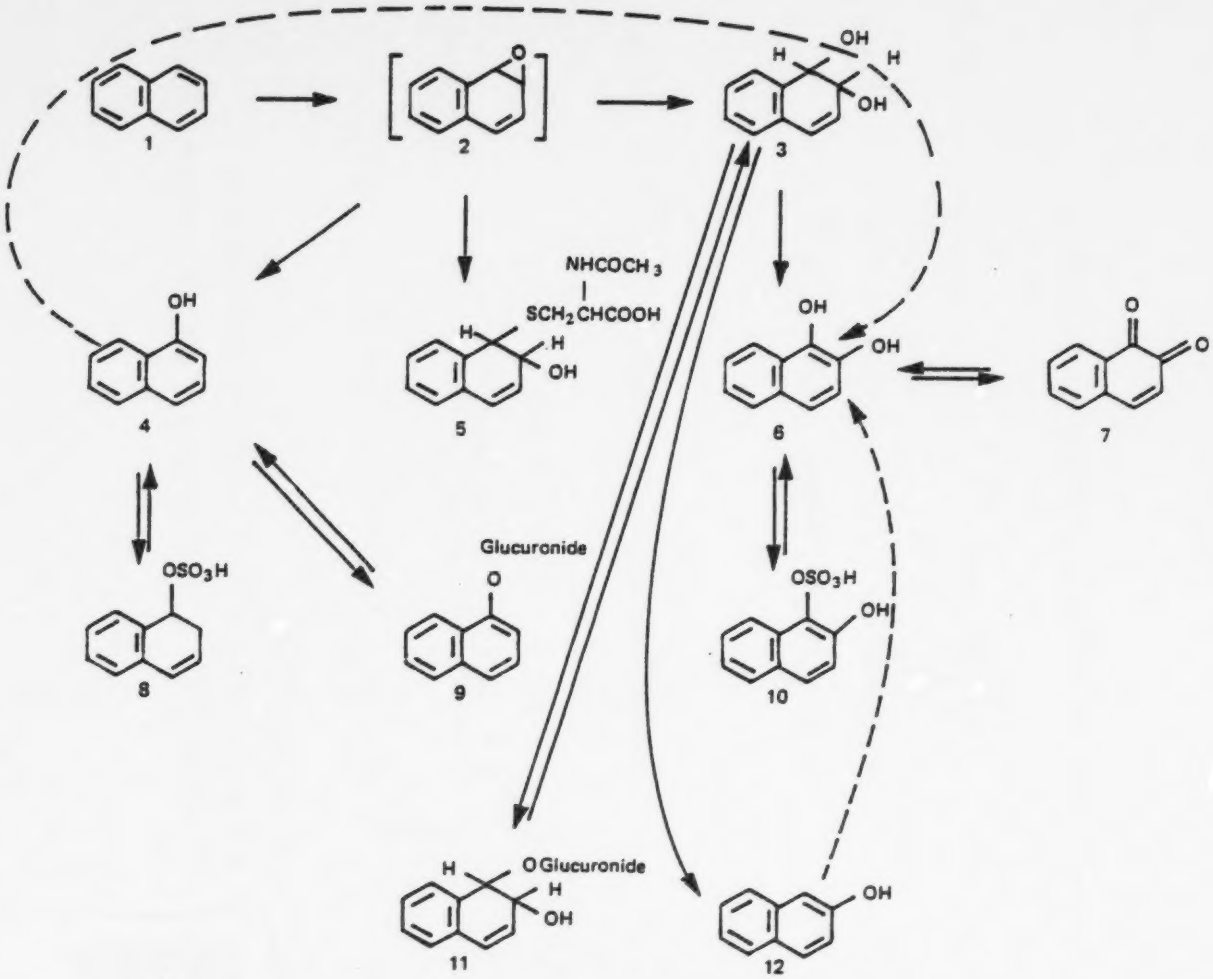
1
O
2
H
OH
H
OH
3
NHCOCH 3
SCH2CHCOOH
H
H
OH
5
OH
4
OH
OH
6
O
O
7
OSO3H
8
Glucuronide
O
9
OSO3H
OH
10
H
O Glucuronide
H
OH
11
OH
12

FIGURE 3-5 METABOLISM OF NAPHTHALENE

Note: (1) Naphthalene; (2) naphthalene epoxide; (3) 1,2-dihydro-1,2-dihydroxynaphthalene (naphthalene diol); (4) 1-naphthol; (5) N-acetyl-S-(1,2-dihydro-2-hydroxynaphthyl) cysteine; (6) 1,2-dihydroxynaphthalene; (7) 1,2-naphthoquinone (β-naphthoquinone); (8) 1-naphthyl sulfate; (9) 1-naphthyl glucuronide; (10) 2-hydroxy-1-naphthyl sulfate; (11) 1-glucosiduronide of (3); (12) 2-naphthol.

Source: Van Heyningen (1979).

TABLE 3-25. DATA ON CARCINOGENICITY OF NAPHTHALENE IN ANIMALS

Species	Route/Dosage	Findings			Reference
			Test	Control	
rat	[a,b]Subcutaneous/ 500 mg/kg, every other week for total of 7 treatments, observed for 18 months	Lymphosarcoma	5/34	1/32	Knake (1956)
		Other Malignant Tumors	0/34	0/32	
mouse	[a,c]Skin painting/ 0.5% naphthalene in benzene, 5 days/ week for lifetime	Lymphocytic Leukemia	4/25	0/21	Knake (1956)
		Lung Adenoma	3/25	1/21	
rat (BD I and BD II)	Oral/10 g/rat "over a period of time"	None of 28 rats developed tumors Rats followed for up to 1000 days			Druckrey and Schmahl (1955)
	Subcutaneous/ 820 mg/rat	None of 10 rats developed tumors.			

---

[a] Coal tar naphthalene contained 10% unknown impurities.

[b] Carbolfuchsin, a known carcinogen, was applied to the site prior to each injection.

[c] Benzene has shown to be an animal carcinogen (Maltoni and Scarnato 1979) and may have contributed to these findings.

are equivocal with respect to the role of naphthalene because: an estimated 10% of the coal tar naphthalene used in the study consisted of an unknown impurity; carbolfuchsin, a known carcinogen, was applied to the site prior to each subcutaneous injection; and the skin-painting experiment utilized benzene, a known animal carcinogen (Maltoni and Scarnato 1979), as the solvent. Several other skin-painting studies were negative for naphthalene (Kennaway 1930, Kennaway and Hieger 1930, Bogdat'eva and Bid 1955).

Mutagenicity

Consistent with its apparent non-carcinogenicity, naphthalene was not mutagenic in bacterial mutagenicity assays (Table 3-26). In vitro cell transformation assays were also negative (Table 3-27).

Teratogenicity

Retarded cranial ossification and heart development were observed in twice as many rats from Sprague-Dawley dams injected intraperitoneally with 395 mg naphthalene/kg bodyweight on days 1-15 of gestation compared to controls ($p<0.001$). No additional information was presented in the meeting abstract (Harris *et al*. 1979).

A metabolite of naphthalene, 2-naphthol, when given to pregnant rabbits (dose, route and time of administration not indicated) caused cataracts and evidence of retinal damage in the newborn (Van der Hoeve 1913). The capability of naphthalene to induce cataracts is discussed below.

Reports of toxicity to newborn infants subsequent to maternal exposure to naphthalene were cited in the criteria document on naphthalene (U.S. EPA 1980a); however, details on dose and effects were not discussed.

Acute and Subchronic Toxicity

The oral LDLo (lowest dose reported to cause lethal effects) for naphthalene in children was reported to be ∿100 mg/kg (Sax 1979). In rodents, the oral LD_{50} (dose reported to be lethal to 50% of the subjects) is in the vicinity of 2000 mg/kg (U.S. EPA 1980a). Long-term sequelae to acute, sublethal exposures to naphthalene in humans include cataracts, sometimes accompanied by retinopathy, and hemolysis, which can lead to jaundice and renal disease from precipitated hemoglobin. These effects have been reported in both infants and adults (U.S. EPA 1980a).

Near blindness developed within 8 to 9 hours in a 36-year-old pharmacist who ingested 5 g (∿80 mg/kg) naphthalene; bilateral cataracts was also reported by Ghetti and Mariani (1956) who examined 21 workers exposed to naphthalene. Details on severity, control incidence, and exposure levels were not indicated in the criteria document (U.S. EPA 1980a).

TABLE 3-26. MUTAGENICITY OF NAPHTHALENE IN VARIOUS *IN VITRO* MICROSOMAL/MAMMALIAN ASSAY SYSTEMS

System	Strain	Result	Reference
Rat microsome/ *Salmonella typhimurium*	TA100	Negative[a]	McCann *et al*. (1975)
	TA1535	Negative[a]	McCann *et al*. (1975)
	TA 1537	Negative[a]	McCann *et al*. (1975)
	TA 98	Negative[a]	McCann *et al*. (1975)
	TM 677	Negative[b]	Kaden *et al*. (1980)
Mouse microsome/ *Salmonella typhimurium*[c]	G46	Negative	Kraemer *et al*. (1974)
Mouse microsome/ *Escherichia coli*	K12	Negative	Kraemer *et al*. (1974)

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[a] Tested at 10, 100, 500, and 1000 μg/plate.

[b] Tested at 2 mM concentration.

[c] Naphthalene-1,2-oxide used in the test system.

TABLE 3-27. ACTIVITY OF NAPHTHALENE WITH *IN VITRO* NEOPLASTIC TRANSFORMATION TEST SYSTEMS

Test System	Dose (µg/L)	Result	Reference
Rat embryo cells/pretreated with Rauscher leukemia virus[a,b]	50	Negative	Freeman *et al*. (1973)
	1,000	Negative	Freeman *et al*. (1973)
	5,000	Negative	Freeman *et al*. (1973)
	10,000	Negative	Freeman *et al*. (1973)
	50,000	Negative	Freeman *et al*. (1973)
	100,000	Negative	Freeman *et al*. (1973)
Mouse embryo cells/pretreated with AKR leukemia virus[a,b]	100	Negative	Rhim *et al*. (1974)
	500	Negative	Rhim *et al*. (1974)
	1,000	Negative	Rhim *et al*. (1974)
	5,000	Negative	Rhim *et al*. (1974)
Mouse mammary gland whole organ culture[c]	1	Negative	Tonelli *et al*. (1979)
	10	Negative	Tonelli *et al*. (1979)
	100	Negative	Tonelli *et al*. (1979)
	1,000	Negative	Tonelli *et al*. (1979)

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[a] In addition to transforming ability, treated cells were injected into newborn rats or mice, respectively, without any evidence of tumorigenicity.

[b] Dissolved in acetone.

[c] Dissolved in dimethylsulfoxide.

Cataracts and retinopathy have been produced in experimental animals at dose levels of ~1000 mg/kg/day, although the onset of lens and retinal changes was noted to occur as early as 1 and 2 days. We were unable to determine the steepness of the dose-effect relationship and the level of a threshold dose from the available data.

The biomolecular mechanisms by which naphthalene induces cataracts in rabbits have been studied by Van Heyningen and coworkers (1967, 1970, 1976, 1979). Reactive metabolites, 1,2-dihydroxynaphthalene and 1,2-naphthoquinone, are formed in the eye, then combine irreversibly with thiol groups of lens protein to form a brown precipitate, resulting in degenerative changes in lens epithelium. Hydrogen peroxide and oxalic acid are formed, and NADPH levels are depleted as the 1,2-dihydrodiol and the quinone are interconverted. Hydrogen peroxide and oxalic acid deplete reduced glutathione (GSH), which normally acts as a metabolic "scavenger" of toxic metabolites that react with thiol groups.

Hemolytic anemia caused by naphthalene exposure seems to be associated with a relative deficiency of enzymes responsible for maintaining GSH, lowering its availability. In the absence of GSH, oxidative denaturization of hemoglobin occurs, leading to stiffening and consequent fragility of red blood cell membranes. Relative deficiencies in the glucose-6-phosphate dehydrogenase (G6PD), which is necessary for maintenance of GSH levels in red blood cells, are known to occur in certain population groups, e.g., blacks who trace their ancestry to malaria hyperendemic areas (Goldstein 1974). Approximately 100 million people worldwide have G6PD deficiency (Wintrobe et al. 1974).

A total of 24 cases of naphthalene-related hemolytic anemia were reported in the world literature between 1920 and 1958; 80% of these cases occurred in blacks or Orientals; three cases involved newborn infants (Dawson et al. 1958). Anecdotal reports suggest an increased susceptibility of newborn infants (1-2 weeks) to the hemolytic effects of naphthalene (Schafer 1951, Cock 1957, Zinkham and Childs 1957). In a review of two cases, in which infants were wrapped in clothing heavily impregnated with either naphthalene or naphthol, Dawson et al. (1958) noted that the affected newborns, as well as one to several other members of the immediate family, showed signs of G6PD deficiency. Along with the genetic susceptibility of these infants, several other factors may have contributed to the production of hemolytic anemia. These include: (1) the application of baby oil to the skin of both infants prior to dressing , thus increasing the absorption of these highly lipid-soluble materials; (2) the reduced thickness of skin in newborns; (3) the diminished glutathione reductase levels normally found in all newborn infants; and (4) a decreased capacity of conjugation with glucuronide in the newborn, thus allowing an accumulation of toxic metabolites (1,2-dihydroxynaphthalene and 1,2-naphoquinone) (Dawson et al.1958).

The dose-effect relationship between naphthalene and hemolytic anemia is not clear. It would appear that in a healthy but G6PD deficient adult low level exposure to naphthalene would lead to shortened life for red blood cells, but this effect could be readily compensated by increased production of red blood cells. Dose-effect relationships cannot be estimated from the anecdotal reports of young infants having toxic reactions to naphthalene vapors from clothing which had been stored in naphthalene moth flakes.

Ambient Water Quality Criterion - Human Health

There are no adequate chronic toxicity or epidemiological studies available for use as a basis for a naphthalene water criterion. The U.S. EPA (1980a) has, therefore, established that a satisfactory criterion for naphthalene cannot be derived at this time.

Other Risk Considerations

There are few quantitative data on carcinogenic or long-term effects of naphthalene exposure. The chemical appears to be absorbed readily by all routes of exposure, but the extent of absorption is not clearly defined. The two major effects linked to naphthalene exposure include cataract formation and hemolytic anemia. Information on the production of cataracts is mainly anecdotal, but a single report noted an effect following ingestion of ~80 mg/kg. Individuals with relative deficiencies in the enzymes needed to maintain reduced glutathione levels, as well as the fetus and young infants (1-2 weeks old), appear at increased risk to develop hemolytic anemia, which can lead to renal damage. Dose-response relationships, however, are unclear.

3.3.2 Human Exposure

3.3.2.1 Introduction

Few monitoring data are available for naphthalene. (See Section 3.2.4.) The major source of human exposure is probably through the use of naphthalene-containing mothballs, involving both inhalation and dermal routes. This section examines the various exposure routes (ingestion, inhalation, and dermal contact) to the extent permitted by the available data.

3.3.2.2 Ingestion

Drinking Water

Naphthalene has only rarely been found in drinking waters. It was detected, but not quantified in a few samples in the National Organics Monitoring Survey (U.S. EPA 1978). In addition, it has been reported that drinking water supplies contain up to 1.4 μg/l (U.S. EPA Region IV, unpublished data). These data are inadequate to provide a good estimate of exposure through drinking water. However, assuming a maximum concentration of 1.4 μg/l and a 2-liter daily intake, a maximum exposure of 2.8 μg/day can be estimated, but it is not known how widespread such exposures might be.

Food

Data for naphthalene in food have not been reported (U.S. [illegible] 1980a). However, the bioaccumulation factor (BCF) of 10.5 calculated by the U.S. EPA (1980a) suggests that accumulation would occur in food items consumed by humans. There is some controversy, however, regarding the potential for accumulation since naphthalene may be rapidly metabolized. Assuming an ambient water concentration of 2 μg/l (U.S. EPA 1980a), a BCF of 10.5, and a fish consumption of 21 g/day (U.S. DA 1978), a possible exposure of 0.4 μg/day can be estimated. This represents a worst-case assumption, since naphthalene has not actually been detected in food items.

3.3.2.3 Inhalation

Krstulovic et al. (1977) reported total naphthalene concentrations of 0.35 ng/m^3 in urban air in Providence, Rhode Island and 0.06 ng/m^3 in suburban and rural air in Kingston and Narragansett Bay, Rhode Island. Assuming these concentrations to be representative, and taking an average respiratory flow of 20 m^3/day (ICRP 1975), estimated exposures are 0.007 μg/day and 0.001 μg/day, respectively.

Inhalation exposure to naphthalene also results from smoking (Akin et al. 1976). Schmeltz et al. (1976) measured about 3 μg resulting in the mainstream smoke of a 85-mm commercial U.S. nonfilter cigarette, and 46 μg resulting in the sidestream smoke. Thus, exposure of smokers to naphthalene could range from 3 to 300 μg/day assuming a range of consumption of 1-100 cigarettes per day (U.S. DHEW 1979). The extent of this exposure may vary with the type of cigarette smoked and the amount inhaled, as well as the number of cigarettes smoked. An estimated 33.2% of adults over 17 years old smoke cigarettes or 54.1 million persons in the United States. Of smokers, 25-30% smoke more than 25 cigarettes per day (U.S. DHEW 1979); thus a large segment of the population could be exposed to naphthalene in the 75- to 300-μg/day range.

In addition, nonsmokers may be exposed to naphthalene through inhalation of sidestream smoke. Although no measurements of naphthalene have been taken in smoke-filled rooms, concentrations may be estimated from measurements of CO levels, which have been summarized by Burns (1975). The results are not consistent, but apparently depend upon a number of variables. They show levels of 44 to 92 mg/m^3 CO in rooms (38-93 m^3) where 30-80 cigarettes had been smoked with no ventilation. The Surgeon General's Report (U.S. DHEW 1979) reported levels up to 50 mg CO produced in sidestream smoke per cigarette, as compared to the 46 μg naphthalene produced per cigarette. Thus, by analogy, a room concentration of up to 83 μg/m^3 can be calculated. Alternatively, using 46 μg naphthalene/cigarette, and assuming a room size of 48 m^3 with no ventilation in which 40 cigarettes were smoked, a concentration of about 38 $\mu g/m^3$ can be calculated. A nonsmoker exposed to such a situation 2 hours/day would receive about 140 μg/day to 300 μg/day, assuming a respiratory flow of 1.8 m^3/hr. Smokers in the same situation would receive a combined exposure from sidestream and mainstream smoke.

There are problems with using CO levels to estimate naphthalene levels in a smoke-filled room since they would be due to sidestream smoke and exhaled mainstream smoke. In addition, the concentration of CO and naphthalene would be influenced by type and amount of tobacco smoked, extent of inhalation, size of room, ventilation, and duration of exposure. The estimates provided above are probably on the high side since worst-case assumptions were frequently made. It appears, however, that concentrations of naphthalene in smoke-filled rooms do not exceed the OSHA standard of 50 mg/m^3 as a time-weighted average.

Inhalation exposures may also occur through the use of naphthalene mothballs. About 26 million households use mothballs; not all contain naphthalene (U.S. EPA 1908b). According to section 3.1, about one-third of the moth repellents produced in the U.S. contain naphthalene. Therefore, this could represent an exposure route to a large sub-population.

Estimated concentrations of naphthalene in air resulting from this use were derived using monitoring data for 1,4-dichlorobenzene (also used as a moth repellent) and assuming the concentration of naphthalene to be comparable when the two saturation vapor concentrations are taken into account. This estimation also assumes that the application rates are the same. The results are shown in Table 3-28. Using the estimated bedroom concentration of 7 $\mu g/m^3$ and assuming a respiratory flow of 20 m^3/day, an intake of 140 μg/day can be calculated. This estimate may be high since a continuous 24-hour exposure to these levels is unlikely. However, effects have been observed resulting from this use, suggesting that it is a significant route of exposure in some cases.

3.3.2.4 Dermal Contact

The use of naphthalene-containing mothballs represents the primary route of dermal exposure; handling of wood products treated with preservatives that contain naphthalene may be an additional source of dermal exposure. The extent of significance of exposures via the dermal route is unknown.

3.3.2.5 Overview

It is apparent that very little information is available regarding human exposure to naphthalene. Estimated exposures are shown in Table 3-29. Most of these estimates provide only a rough idea of exposure. Naphthalene is rarely detected in drinking water; intake through food has been calculated by using a bioconcentration factor. It is difficult to identify the predominant route of exposure for the general population, but inhalation of ambient air appears to be a relatively minor route of exposure. Smokers clearly receive the largest exposures, although nonsmokers present in a smoke-filled room can receive comparable exposures. The use of naphthalene moth repellents may also result in relatively high indoor air concentrations.

TABLE 3-28. ESTIMATED AIR CONCENTRATIONS RESULTING FROM NAPHTHALENE USE AS A MOTH REPELLENT

Compound	Saturation Vapor Concentration (g/m^3)	Air Concentration (μg/m^3)	
Dichlorobenzene	9	wardrobe	1700[a]
		closet with wardrobe	315[a]
		associated bedroom	105[a]
Naphthalene	0.62	wardrobe	117[b]
		closet with wardrobe	22[b]
		associated bedroom	7[b]

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[a] Measured concentration (Morita and Ohi, 1975).

[b] Estimated concentration.

TABLE 3-29. ESTIMATED UPPER LIMIT HUMAN EXPOSURES TO NAPHTHALENE[a]

Route	Exposure (μg/day)
Ingestion	
Drinking water	2.8 maximum
Food-fish	0.4 maximum
Inhalation	
Ambient Air	
Urban	0.007
Rural/suburban	0.001
Bedroom-with mothball use	140
Smoker (1-100 cigarettes/day)	3-300
Non-smoker in smoke filled room	140-300 (2-hour exposure)
Occupational (at OSHA standard)	∿500,000 (8-hour exposure)

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[a] For assumptions see text. Please note that all of these estimates are based upon very limited data, and are not necessarily representative of typical exposures.

3.4 EFFECTS AND EXPOSURE -- AQUATIC BIOTA

3.4.1 Effects on Aquatic Organisms

3.4.1.1 Introduction

Aquatic toxicity data are limited for naphthalene; some of the available data are the results of static bioassays in which concentrations are measured only at the initiation, not during the course, of the experiment. Since naphthalene rapidly volatilizes and biodegrades, the results of these studies may tend to underestimate the toxicity of naphthalene by not accounting for loss of the compound during a test. Aquatic species tested include fish, invertebrates, and plants from both marine and freshwater systems.

3.4.1.2 Freshwater Organisms

Acute toxicity data for naphthalene are presented in Table 3-30; LC_{50}'s (concentrations lethal to 50% of test organisms) range from 0.92 mg/l to 150 mg/l. The most sensitive of the five animal species tested were pink salmon fry (0.92 mg/l) and rainbow trout (2.3 mg/l).

The only freshwater chronic study available was an embryo-larva test for the fathead minnow. A chronic value of 0.62 mg/l (limits 0.45-0.85 mg/l) was measured (U.S. EPA 1980a).

Several studies have demonstrated the sublethal effects of naphthalene to aquatic organisms. The feeding rate of copepods (*Eurytemora affinis*) was reduced by 10% and 16% following 24-hours' exposure to 1 mg/l and 2 mg/l naphthalene, respectively. Prolonged exposure at lower concentrations (10 days at 10 µg/l and 50 µg/l) resulted in an increase in mortality and decrease in egg production and feeding rate of these copepods (Neff 1979). Studies of sublethal effects in pink salmon fry (*Onchorhynchus gorbauscha*) indicated that at a naphthalene concentration of 0.76 mg/l, oxygen consumption and the breathing rate increased sharply. However, with continued exposure, both oxygen consumption and breathing rate decreased (Thomas and Rice 1978).

Freshwater algae are less sensitive than are fish to naphthalene; in studies on the green algae *Chlorella vulgaris*, growth and reproduction were inhibited by concentrations of between 3.3 and 30 mg/l (Kauss and Hutchinson 1975); the fifty percent effects concentration (EC_{50}) was 33 mg/l. Photosynthetic activity was inhibited at 30 mg/l in 89% of a test culture of the algae *Clamydomonas angulosa* (Kauss *et al*. 1973).

3.4.1.3 Marine Organisms

Acute toxicity values for saltwater biota are comparable to those measured for freshwater organisms (Table 3-30). With the exception of the Pacific oyster (*Crassostrea gigas*) with an acute effects level of 199 mg/l, the acute values ranged from 2.3 mg/l (grass shrimp) to 3.8 mg/l (polychaete worm).

TABLE 3-30. ACUTE TOXICITY OF NAPHTHALENE FOR AQUATIC SPECIES

Species	Method[a]	LC_{50}(mg/l)	Reference
		Freshwater Species	
Cladoceran *Daphnia magna*	S,U	8.5	U.S. EPA (1978)
Rainbow trout *Salmo gairdneri*	FT,M	2.3	Degraeve *et al*. (1980)
Fathead minnow *Pimephales promelas*	FT,M	4.9	Degraeve *et al*. (1980)
Mosquitofish *Gambusia affinis*	FT, M	150.0	Wallen *et al*. (1957)
Pink salmon (fry) *Onchorhynchus gorbuschi*	-	0.92	Thomas and Rice (1978)
		Saltwater Species	
Polychaete *Neanthes aranaceodentata*	S,U	3.8	Rossi and Neff (1978)
Pacific oyster *Crassostrea gigas*	S,U	199.0	Legor (1974)
Grass shrimp *Palaemonetes pugio*	S,M	2.3 2.4	Tatem (1975) Neff *et al*. (1976)
Crown shrimp *Panaeus aztecus*	-	2.5	Anderson *et al*. (1974)
Sheepshead minnow *Cyprinodon variegatus*		2.4	Anderson *et al*. (1974)
Amphipod *Elasmopus pectenicrus*	-	2.7	Lee and Nicol (1978)
Dungeness crab (zoeae) *Cancer magister*		>2.0	Caldwell *et al*.(1977)

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[a] S=static; FT=flow through; M=measured; U=unmeasured

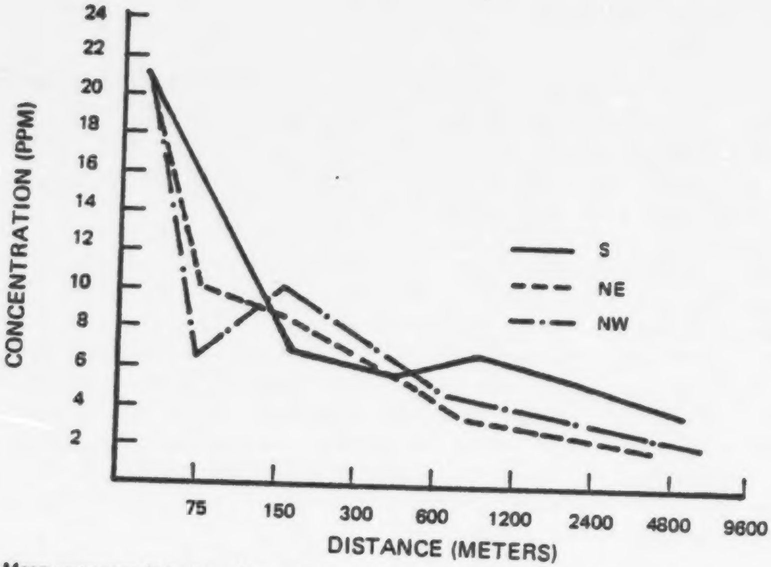
Certain sublethal effects have been attributed to even lower concentrations. The blue crab (Callinectes sapidus) was found to be able to detect naphthalene, as indicated by certain behavior, at concentrations of 0.12 mg/l (Pearson and Olla 1979). Naphthalene also induced sublethal effects in zooeal stages of Dungeness crabs (Cancer magister) at concentrations of 0.13 mg/l (Neff 1979). Histopathologic changes, specifically necrosis of tastebuds, were found in the estuarine fish mummichog at concentrations from 2 μg/l to 20 μg/l.

In a field study, Armstrong et al. (1979) looked at the relationship between sediment naphthalene concentration and the presence of biota in the vicinity of an oil separator rig in Trinity Bay, Texas. They found an inverse correlation between naphthalene concentrations in sediment and numbers of benthic organisms. Figure 3-6 shows the relationship between sediment concentrations and number of organisms collected at corresponding distances in different directions from the separator platform. The first station, 15 m. from the rig, had the highest concentration of naphthalene (approximately 21 mg/l, see Figure 3-6), and the area was almost completely devoid of organisms. At 75-150 m from the rig the concentrations dropped significantly while the benthic populations were improved slightly, although still depressed. The populations were at or above control levels at 685 m to 1675 m from the rig at which point naphthalene concentrations were <7 mg/l. The authors hypothesized that a low (possibly 2 mg/l) persistent concentration of naphthalene is capable of restricting many marine species (Armstrong et al. 1979).

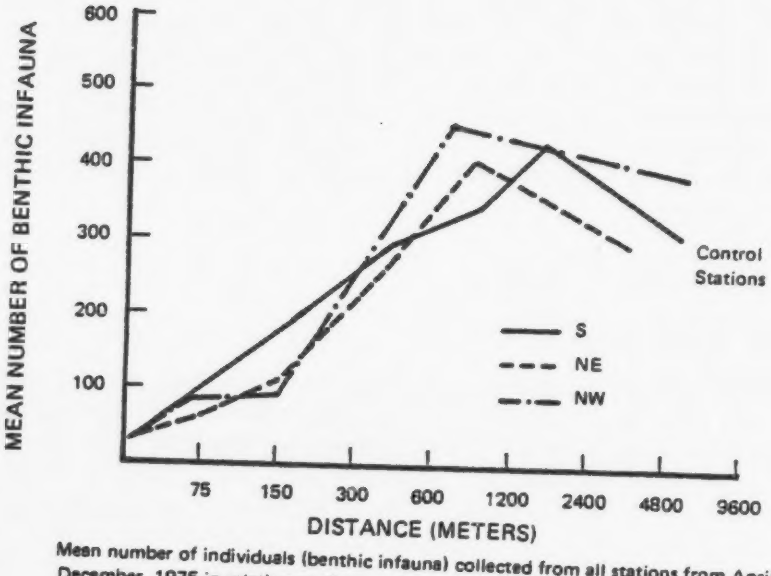
3.4.1.4 Factors Affecting Toxicity

Some studies have been conducted of the relationship between various environmental factors and the toxicity of PAHs in general, and naphthalene in particular. The factors most extensively studied have been salinity and temperature.

Temperature could affect the survival of aquatic organisms exposed to compounds such as PAHs in at least three ways: (1) by changing the rate of loss from the waterbody through volatilization and biodegradation, thus altering the persistence of these compounds in water; (2) by affecting the sensitivity of the organism by changing rates of hydrocarbon uptake, metabolism, and depuration of metabolites and parent compound; and (3) by placing additional stress on an organism through exposure to temperatures that deviate from its optimal range. Compounds such as PAHs probably remain at toxic concentrations for longer periods of time at lower temperatures because of reduced volatility and biodegradation of aromatic compounds in water. However, generalizations about the direction (increasing or decreasing) and magnitude of the effects of temperature changes on fish exposed to specific PAHs cannot be made. The data of Korn et al. (1979) indicated that for pink salmon, naphthalene threshold limit values (TLV) did not vary significantly between 1°C and 12°C. In shrimp, naphthalene was two times more toxic (as measured by the TLV) at 12°C than at 1°C.



Mean concentration of total naphthalenes in sediments for stations in Trinity Bay in relation to distance from the C-2 Separator Platform for the months of December, 1974-December, 1975.



Mean number of individuals (benthic infauna) collected from all stations from April, 1974–December, 1975 in relation to distance from the brine discharge.

FIGURE 3-6 **MEAN NAPHTHALENE CONCENTRATIONS IN SEDIMENTS AND MEAN NUMBERS OF BENTHIC ORGANISMS AS FUNCTIONS OF DISTANCE FROM AN OIL SEPARATOR RIG IN TRINITY BAY, TX.**

Note: (For both graphs, each line represents a separate sampling transect emanating from the pollutant source in the direction indicated.)

Source: Armstrong *et al* (1979)

The effect of salinity on the toxicity of PAHs has also been investigated. The toxicity of four concentrations (0, 125, 250 and 500 µg/l) of naphthalene at three salinities (5, 15, and 25 parts per thousand, ^{o}/oo was tested on zoeae of the mud crab Rhithropanopeus harrisii. Survival was high at 125 µg/l and 250 µg/l for all salinities and at 500 µg/l in 15 and 25 ^{o}/oo S; but at 5 ^{o}/oo salinity, fewer organisms survived. Naphthalene also increased the development rate of the larvae (Laughlin and Neff 1979). Experiments on mummichog (Fundulus heteroclitus), a euryhaline, estuarine fish, also show the influence of salinity. Levitan and Taylor (1979) tested five salinities (2, 8, 15, 23 and 33 ^{o}/oo) and concentrations of 4 mg/l and 6 mg/l naphthalene. At 6 mg/l, survival was greatest at 8 ^{o}/o S and 15 ^{o}/o S, and it decreased at the salinity extremes. At a concentration of 4 mg/l, survival was greater at lower salinities than at high. Thus, as with temperature, salinity-toxicity interactions do not necessarily occur in a uniform, predictable manner.

3.4.1.5 Ambient Water Quality Criterion

At this time, there is no ambient water quality criterion for naphthalene for the protection of either freshwater or saltwater aquatic life. This is due to a lack of sufficient toxicity data on which to base the criterion. However, the criterion document (U.S. EPA 1980) states that acute and chronic toxicity to freshwater life may occur at concentrations as low as 2.3 mg/l and 0.62 mg/l, respectively. Acute toxicity to saltwater life may occur at concentrations as low as 2.4 mg/l; no chronic data were available. The criterion document also points out the possibility that there are more sensitive species than those tested.

3.4.2 Exposure of Aquatic Biota

3.4.2.1 Monitoring Data

The STORET water quality data base for naphthalene is very limited. Data were available for ambient and effluent water, sediment, and fish tissue, but there were very few unremarked observations in each of these categories. The range of concentrations for the unremarked data were described in Tables 3-22 and 3-23, and are briefly summarized below.

Sample Source	Unremarked Data: No. Observations	Range of Values
Ambient water	8	≤1.0-100 µg/l
Effluent water	68	≤1->1000 µg/l
Sediment	21	0.02-496 µg/kg

Most of the STORET data, particulary for ambient water, were remarked; i.e., the values were either detection limits or the actual value was less than that indicated. Fifty-two percent (52%) of the remarked naphthalene observations ranged from 0.005 to 17 µg/l. The unremarked sediment levels are generally higher than ambient water level concentration, which illustrates the tendency of naphthalene to accumulate in the sediments over time.

3.4.2.2 EXAMS

EXAMS modeling data indicate that of the six aquatic systems analyzed, the only system in which a majority of the naphthalene went to the sediments was the pond; naphthalene was almost equally divided between sediments and water in the coastal plain river, and distributed to a greater extent in water than in sediments in the other rivers and lakes (>78% in water column). In all six environments, fate processes such as volatilization, photolysis, and biotransformation are all significant, and, thus, in water naphthalene would not persist as the parent compound for very long. However, once naphthalene is in the sediments, it tends to persist and is lost at a rate five times less than that of naphthalene in water.

The EXAMS modelling data indicate that, based on a loading rate of 0.2 kg/hr, an approximate discharge rate from a coal-tar plant, the highest naphthalene concentrations in water would be in the pond (0.48 mg/l). It is not likely that such a discharge would occur directly into a pond ecosystem.

3.4.2.3 Factors Affecting Bioavailability of Sediment Concentrations

The various factors that affect partitioning of naphthalene between water and sediments are discussed in Section 3.2.3.4. It is known that aquatic biota are exposed to naphthalene directly from water, but the extent to which they may be exposed to sediment concentrations of this compound is less well understood.

Several laboratory and field studies have been conducted to determine the extent of uptake of naphthalene from sediments by aquatic organisms. The organisms most often studied include deposit feeders such as polychaete worms (*Neanthes arenaceodentata*), (*Phascolosoma agassizii*), and clams (*Rangia cuneata*, *Macoma inquinata*), and the suspension feeding clam *Protothaca staminea*. Accumulation of naphthalene was noted in all of these organisms, but depuration was rapid and nearly total upon removal to clean water (Neff 1979). Accumulation of hydrocarbons, including naphthalenes from oil-contaminated sediments by the English sole *Paraphrys vetulus* has also been investigated (McCain *et al*. 1978). Results from several separate studies (Roesijadi *et al*. 1978, Fucik *et al*. 1977, Anderson *et al*. 1977) indicate that overall uptake of PAHs is not significant, but is greater by suspension feeders than deposit feeders, and that accumulation by fish is greater from water than from sediment. The conclusion has been made that the source of PAH taken up is, to a greater extent, PAH in interstitial waters (dissolved) and in the water column (dissolved and/or adsorbed onto suspended solids), rather than PAH desorbed from the sediment itself (Neff 1979).

These studies also indicated that sediment adsorbed PAHs are not readily metabolized by benthic invertebrates. However, based on the few species studied, it is apparent that benthic organisms could take up naphthalene from sediment and interstitial waters to a moderate degree since the dynamics of desorption of naphthalene from sediment to water are not well understood; so, it is impossible to quantify the degree to which accumulation of PAHs in sediment represents a major source of exposure to aquatic biota.

3.4.3 Summary - Aquatic Effects and Exposure

Naphthalene concentrations at which acute toxic effects have been reported for aquatic organisms range from 0.92 mg/l to 199 mg/l. Certain sublethal effects (behavioral) on aquatic organisms have been observed at concentrations as low as 0.12 mg/l; histopathologic changes were noted in estuarine fish at concentrations from 0.002 mg/l to 0.02 mg/l. A chronic effects value of 0.62 mg/l was obtained in an embryo-larva test conducted on fathead minnows. Monitoring data for naphthalene indicate that the levels in ambient waters are generally about 10 μg/l; sediment levels range from 0.02 μg/kg to less than 500 μg/kg.

3.5 RISK CONSIDERATIONS

3.5.1 Introduction

The purpose of this section is to evaluate potential risks to humans and aquatic biota resulting from exposure to naphthalene in the environment. This risk analysis is hampered by the scarcity of quantitative data on health effects levels, and by the very limited amount of monitoring data and other information available to use as an indication of the extent of exposure. All data reviewed in this section are presented in more detail in the preceeding sections of this chapter.

3.5.2 Humans

3.5.2.1 Statement of Risk

There appears to be little risk to the general population as a result of environmental exposure to naphthalene. Although this compound has been linked with cataract formation and hemolytic anemia, the levels at which these effects have been observed are considerably higher than the maximum estimated human intake levels. There are several orders of magnitude separating the maximum estimated exposure to certain subpopulations via smoking or mothball usage, and the lowest level at which acute human effects have been observed. On the basis of the available monitoring data, the estimated daily exposure to the general population via ingestion of water and food and inhalation of ambient air is at least five orders of magnitude less than the lowest reported toxic dose (the LDL reported for children was 100 mg/kg, or ~1000 mg).

3.5.2.2 Discussion

Naphthalene appears to be absorbed via all routes of exposure (ingestion, inhalation, and skin contact), but the extent of that absorption has not been defined. The two major effects of naphthalene exposure are hemolytic anemia and cataract formation; individuals with deficiencies in the enzymes needed to maintain reduced glutathione levels, as well as the fetus and newborn, are at an increased risk of developing hemolytic anemia.

Studies on the chronic effects of naphthalene have generally been negative. This substance has not been shown to be carcinogenic, or mutagenic; anecdotal reports of teratogenicity were cited (U.S. EPA 1980a). Accidental ingestion of large amounts of naphthalene was reported to have caused near blindness, demonstrating the potential for severe adverse effects.

The sources of naphthalene to which the general population is exposed represent very small intake levels: up to 2.8×10^{-3} mg/day from ingestion of drinking water; up to 0.4×10^{-3} mg/day from consumption of contaminated fish; and up to 7×10^{-6} mg/day from inhalation of ambient air. There are, however, a number of subpopulations exposed to much higher levels in air. Heavy smokers (about 10% of U.S. adults) may be exposed to levels in mainstream smoke up to 0.3 mg/day; nonsmokers in a smoke-filled room may be exposed to similar levels. On the basis of assumptions outlined in Section 3.3.1, inhalation exposure due to mothball usage may be as high as 0.14 mg/day. (It has been estimated that 26 x 10^6 households use mothballs; only one-third contain naphthalene.) An additional major source of exposure is the occupational environment, but quantification of that exposure route is beyond the scope of this report. Since naphthalene is potentially toxic via inhalation, these scenarios may pose some level of risk to specific subpopulations.

3.5.3 Aquatic Biota

There is very little information available on the extent of exposure of aquatic biota to naphthalene. However, the available monitoring data suggest that concentrations reported in ambient water are about two orders of magnitude lower than the levels associated with acute or chronic effects to aquatic organisms.

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APPENDIX A

NOTE 1: EPA, 1979g. Raw waste loading of naphthalene from the wood preserving industry is based on the following flows and respective naphthalene concentrations and applying the average to the total number of facilities. Assume 300 day/yr operation.

Plant	Flow (10^6 ℓ/day)	Naphthalene (mg/ℓ)	Naphthalene (kkg/yr)
1,078	0.057	3.14	0.05
1,100	0.236	0.464	0.03
897	0.160	3.47	0.1
591	0.013	34.7	0.1
548	0.122	31.0	1.1
267	0.034	45.0	0.5
		average	0.3

387 plants x 0.3 kkg naphthalene/yr = 116 kkg naphthalene available for discharge/yr.

Waste load % reduction for naphthalene ranges from 50% (current pretreatment technology) to >99% (current BPT). Therefore, about 87 kkg of naphthalene are removed prior to discharge. The remaining 29 kkg are for the most part (95-100%) discharged to POTWs.

NOTE 2: The maximum naphthalene discharge (raw wastewater) of 2 kkg/yr from manufacture of synthetic tanning agents was calculated based on the geometric mean of average naphthalene concentration (µg/ℓ) and a total industry wide flow of 200 x 10^6 ℓ/day, assuming 365 day/yr operation (EPA 1979e).

Subcategory	Naphthalene (µg/ℓ)
1	46
2	49
3	32
4	"present"
5	27
6	"present"
7	26

geometric mean = 24 µg/ℓ

"Present" was assumed to be at the detection limit, 10 µg/ℓ.
24 µg/ℓ x 200 x 10^6 ℓ/day x 365 d/yr = 2 kkg naphthalene

APPENDIX B. APPLICATION OF THE AIR-TO-SURFACE PATHWAY EVALUATION METHOD FOR POLYNUCLEAR AROMATIC HYDROCARBONS

A method has been developed for estimating airborne toxicant deposition rates (air-to-surface pathway evaluation method, Arthur D. Little, Inc., 1981). The method accounts for both wet and dry deposition to land and water surfaces. When deposition to a watershed or other land area is estimated, this can be interpreted as an upper bound on the chemical loading to an associated surface water body resulting from air deposition, since only a fraction of the mass deposited on land surfaces will be delivered to the water body. The air-to-surface pathway evaluation method accounts for the partitioning of an airborne contaminant between adsorbed and vapor phases, with differing deposition rates inferred for the separate phases. It relies on fundamental physicochemical properties and is designed to use available data, while filling in data gaps with estimated values of various parameters. The evaluation method has been applied to naphthalene, anthracene, and benzo[a]pyrene. Each of the three PAHs modeled has an atmospheric chemical degradation of roughly 0.1 hr.$^{-1}$ leading to half-lives of 5-10 hours (Radding _et al_. 1976). Under typical meteorologic conditions this corresponds roughly to the travel time across major urban areas. Since urban areas also would be expected to have much greater emission densities than rural areas, significant urban/rural differences in air concentrations of PAHs are expected, and indeed observed. These factors suggest that deposition rates under urban and rural conditions should be considered separately.

One of the most important chemical properties influencing air-to-surface transfer is the vapor pressure. The vapor pressure affects the partitioning of airborne contaminants between vapor and adsorbed phases. The deposition rate is typically much greater for the adsorbed fraction of the airborne contaminant. The effect of vapor pressure is expressed by equation (5) of the Arthur D. Little report (1981):

$$\phi = \frac{.165\theta}{P_o + .165}$$

where

ϕ is the adsorbed fraction of the total airborne mass,

θ is the available aerosol surface area $\frac{cm^2}{cm^3}$ and

P_o is the saturation vapor pressure of the contaminant at ambient temperature (torr)

The available aerosol surface area is typically greater in urban areas where concentrations of total suspended particulates are higher than in rural areas. In the plume from a combustion source, the aerosol surface area is even higher than typically found in urban air. Application of the above equation results in aerosol partitioning for the three PAHs as shown below:

PAH	Adsorbed Fraction of Total Airborne Mass: Rural	Urban	Near Combustion Sources
Naphthalene	7×10^{-6}	3×10^{-4}	0.02
Anthracene	0.002	0.06	0.97
Benzo[a]pyrene	.99	1.00	1.00

Benzo[a]pyrene is strongly partitioned with the aerosol phase, regardless of ambient conditions, while at the other extreme naphthalene exists primarily as a vapor in the atmosphere. Anthracene exhibits intermediate properties, and the adsorbed fraction is sensitive to ambient conditions.

The dry deposition flux is proportional to the dry deposition velocity, V_d, i.e.,

$$\text{Dry Flux} = V_d \, C_{air}$$

where

C_{air} is the ground-level air concentration.

The dry deposition velocity with respect to the total airborne contaminant is calculated as the (mass) weighted average of the deposition velocity for the vapor and sorbed fractions, i.e.,:

$$V_d = V_{d,s}\phi + V_{d,v}\,(1-\phi) \qquad \text{(Eq. 6 of Arthur D. Little 1981)}$$

According to the air-to-surface pathway method (Arthur D. Little 1981), the respective dry deposition velocities are given below:

	Dry Deposition Velocity				
PAH	$V_{d,v}$ (cm/sec)	$V_{d,s}$ (cm/sec)	Rural	Urban	Combustion Source
Naphthalene	0.04	1	0.04	0.04	0.06
Anthracene	0.02	1	0.02	0.08	1.00
Benzo[a]pyrene	0.02	1	1.00	1.00	1.00

Wet deposition is controlled by the precipitation scavenging ratio, r, which expresses the ratio of pollutant concentration in precipitation (ng/l) to pollutant concentration in air ($\mu g/m^3$). The scavenging ratio is calculated by contributions from the vapor and sorbed fractions, i.e.:

$$r = r_s (\phi) + r_v (1-\phi)$$

where r, r_s and r_v are scavenging ratios for the total airborne mass, the sorbed contaminant, and the vapor phase, respectively. Once the scavenging ratio is known, the wet deposition flux is given by wet flux = rRC_{air}, where R is the rainfall rate. These parameter values have been estimated, as shown below:

	Precipitation Scavenging Ratios				
			r		
PAH	r_s*	r_v	Rural	Urban	Combustion Sources
Naphthalene	6×10^4	53	53	71	2.5×10^3
Anthracene	6×10^4	14	130	3.6×10^3	1.2×10^5
Benzo[a]pyrene	6×10^4	5.4×10^4	6×10^4	6×10^4	1.2×10^5

For the purpose of further analysis a generic urban environment has been modeled on the basis of characteristics of Philadelphia and Cleveland. The average wind speed is 10.25 kts (5.3 m/s) and the annual rainfall is 1.0 m/yr. The urban area is 100 mi^2 (2.6×10^8 m^2).

The generic rural area is defined as a volume of air within which an associated urban source would contribute to rural concentrations. The size of the area is constrained by the half-life in air, such that the concentration is typical of an area significantly affected by the urban source. At a half-life of 5 hours, and typical wind speed of 5.3 m/sec., naphthalene contamination from an urban area could be significant over an area of 10^{10} m^2 (roughly 40,000 square miles).

Median observed ambient concentrations for three PAHs in urban and rural areas are presented below (White and Vanderslice 1980):

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*Tabulated r_s values apply for rural and urban conditions. Near a combustion source the adsorbed phase is expected to be associated with larger particles resulting in a scavenging ratio, $r_s = 1.2\times10^5$.

PAH	Median Observed Concentration ($\mu g/m^3$) Rural	Urban
Naphthalene	$7x10^{-5}$	$5x10^{-4}$
Anthracene	$1x10^{-3}$	$8x10^{-3}$
Benzo[a]pyrene	$1x10^{-3}$	$1x10^{-2}$

Using the pathway evaluation method we have estimated the emission that would result in a specific ambient concentration, given the degradation rate, deposition velocity, rainfall rate, and precipitation scavenging ratio. Applying the equation for wet flux and dry flux we also estimated the amount deposited in the generic rural and urban study areas. Then, by comparison of the deposition rates with emission rates, we estimated the fraction of total atmospheric emissions of each of the three PAHs which would be deposited within the urban and rural study areas. These results are shown below:

PAH	Deposition Rate % of Emissions Dry Deposited Rural	 Urban*	 % of Emissions Wet Deposited Rural	 Urban	 % Deposited Rural	 Urban
Naphthalene	2	2-3	<1	<1	2	2-3
Anthracene	1	4-19	<1	1-7	1	5-26
Benzo[a]pyrene	22	19	4	4-7	26	23-26

From the results above, it is apparent that a very small fraction of atmospheric emissions of naphthalene are deposited on land or water surfaces. The fraction of air emitted anthracene that is eventually deposited is uncertain, but could be fairly large percentage. Approximately one-fourth of all benzo[a]pyrene emitted into the atmosphere will eventually be deposited on land and water surfaces, where it would contribute to the contamination of surface runoff and surface water bodies.

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*The range for urban areas reflects alternative assumptions that the chemical has equilibrated with ambient aerosol or remains associated with particulates in the plume from the combustion zone.

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APPENDIX
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